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GENERAL CHEMISTRY
FOR COLLEGES

BY

ALEXANDER SMITH

Professor of Chemistry, and Head of the Department,
Columbia University

SECOND EDITION
ENTIRELY REWRITTEN

EIGHTY-THIRD
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THE CENTURY CO.
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First Edition, May, 1908
Reprinted October, 1908; April, 1909; May, 1910; May, 1911;
April, 1912; April, 1913; May, 1914; January, 1915
Second Edition, January, 1916
Reprinted July, 1916; August, 1916;
September, 1916; October, 1916
June, 1917; October, 1917

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PREFACE TO THE FIRST EDITION

THE present work differs from the Author's "Introduction to General Inorganic Chemistry" in being intended for pupils who can devote less time to the study of the science, and whose needs can be satisfied by a less extensive course. It resembles the larger work in the arrangement of the contents and in the general method of treatment. The matter, and particularly the theoretical matter, however, has been simplified and has been confined strictly to the most fundamental topics. Such parts of the theory as are thus given, are presented with the same fullness as before, and are illustrated and applied with all the persistence needed to insure full apprehension and, ultimately, spontaneous employment by the student. Such parts as could not be treated in this way, within the limits set by the plan of the book, have been omitted. Methods materially different from those used in the "Introduction" have been employed in presenting many topics. Conspicuous differences of this kind will be noted particularly in the treatment of combining proportions, formulæ and equations, molecular and atomic weights, chemical equilibrium, ionic substances and their interactions, and the theory of precipitation.

The writer desires to express his profound gratitude to the many chemists who have made valuable criticisms and suggestions. Most of these comments applied to the "Introduction to General Inorganic Chemistry," but many of them have been used in preparing this work (General Chemistry for Colleges), and all will be considered in the second edition of the larger book.

For critical reading of the whole of the proofs of the present work, the writer desires especially to thank Messrs. A. T. McLeod and Alan W. C. Menzies of the University of Chicago. Other corrections and suggestions will be gladly received by the author.

ALEXANDER SMITH.

Chicago, April, 1908.

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PREFACE TO THE SECOND EDITION

In preparing the second edition, the entire book has been rewritten. The introduction to the subject has been improved and greatly simplified, and several difficult topics have been transferred to later chapters. The explanations of the theoretical subjects, and of the methods of making calculations have been clarified and additional illustrations have been given. In view of its importance to prospective students of biology and medicine, osmotic pressure is treated in greater detail. To add greater interest to the study of the science, and because of their educational value, the historical references have been expanded, many more applications of chemistry have been discussed, and the number of figures has been considerably increased. Extensive new sections on oxidation and reduction, and on various methods of writing equations, on radio-activity, and on electromotive chemistry have been added. Briefer new sections on atomic numbers, colloids, foods, explosives, water treatment, and many other subjects, have been included. New pedagogical devices have been introduced. So far as recent advances can be apprehended and applied by first-year college students, the treatment has been brought up to date.

The author is greatly indebted to Messrs. P. C. Haeseler, and Herbert E. Eastlack for much assistance in reading the proof and for many valuable suggestions.

Alexander Smith.

New York, January, 1916.

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GENERAL CHEMISTRY FOR COLLEGES

GENERAL CHEMISTRY FOR COLLEGES

CHAPTER I

THE CHEMICAL VIEW OF MATTER

CHEMISTRY is a science which deals with *all* forms of matter. It considers the natural kinds, such as rocks and minerals, as well as materials like fat and flour obtained from animals or plants. It deals also with artificial products like paints or explosives. When we wish information about any specimen or kind of matter, we consult a chemist. Now chemists have worked out a point of view which enables them to attack any problem connected with matter in a systematic manner and to state the results in a clear and simple way. To learn something of chemistry, we must acquire this **point of view** and master the **technical language** the chemist uses in stating and discussing his results.

Properties. — Suppose that a piece of rusty iron is submitted to the chemist. He at once examines the rust and notes that it is solid, reddish-brown in color and earthy in appearance. He separates some of it from the iron and finds it to be brittle, that is, easily broken and capable of being pulverized in a mortar. He finds that its density is about 4.5, that is to say, 1 c.c. (Appendix I) of it weighs about 4.5 g. On heating some of it in a flame, he finds that it does not melt, and must therefore have a very high melting-point. These qualities he calls *properties*, and more especially physical properties. Since all specimens of iron-rust show exactly the same properties, he often calls them **specific physical properties**, because they are **properties shown by all specimens of a particular species of matter.**

After removing any rust by filing or scraping, the chemist examines the iron, and finds a fresh, clean surface to be almost white and metallic in appearance. The metal is tenacious, so that it can be bent but not easily broken. It is ductile and can therefore be drawn out into wire. He finds that its density is about 7.5, and that the metal is incapable of being melted in an ordinary flame. In addition, he finds it to be strongly attracted by a magnet, while rust is not attracted.

The chemist, then, studies what he calls the specific physical properties of each material, in order that he may be able to recognize various materials.

Substances. — All specimens of iron show one set of properties and all specimens of iron-rust show a different set, peculiar to rust. The chemist calls **any definite variety of matter, all specimens of which show the same properties,** a **substance.** Iron is one substance and rust another. A substance is recognized by its properties.

The point of view of the chemist thus consists in describing any material by ascertaining whether it is made up of one, or of more than one substance. **He describes it by naming the substances which,** by a study of their properties, **he has found in it.**

Two Illustrations of the Study and Description of Materials. — If a piece of **granite** is examined by a chemist, he observes at once that it is spotted in appearance, and made up of several crystalline materials of differing nature. He therefore breaks it up and studies the *properties* of the fragments. Some of the fragments of granite are dark and with a penknife can easily be split into transparent sheets, thinner than paper. These particular fragments are in all respects like *mica* (Fig. 1). This substance is a mineral which, in certain neighborhoods, occurs in large masses, and sheets of it ("isinglass") are used to fill the openings in stoves. Others of the fragments are clear like glass, and are very hard (see Appendix II), and have *all* the properties

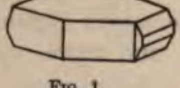

Fig. 1.

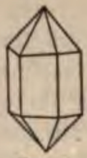

Fig. 2.

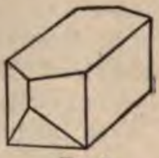

Fig. 3.

of quartz or rock crystal (Fig. 2), which is another substance well known to the chemist. The remaining fragments are less clear than is quartz, and are not so hard. They can be split into layers, but not nearly so easily as can mica. They form oblong crystals, differing in this also from quartz, which shows hexagonal crystals.* This substance is *felspar* (Fig. 3). Thus the chemist studies the physical properties of the fragments, and finds that there are three different substances in granite. He reports that the components of granite are mica, quartz, and felspar.

When **flour** is examined by the chemist, it appears to the eye to be all alike. Under the microscope, even, all he can learn is that it consists largely of grains, which have the characteristic appearance (first property) of grains of starch (see Fig. 108, p. 403). He places some flour on a square piece of cheesecloth and encloses it by tying with a thread (Fig. 4). On kneading the little bag in a vessel of water, the water becomes milky. When the milky water stands, the white material settles to the bottom, the water can be poured off, and the deposit can be dried. This white substance, when boiled with water, gives an almost clear liquid which jellies on cooling. This is another property of starch. A little tincture of iodine (solution of iodine in alcohol), dropped on a part of the starch, causes the latter to turn blue. This is a very characteristic property of (and therefore *test* for) starch. When the bag of flour is kneaded persistently in water which is frequently changed, the material finally ceases to render the water milky. The starch has all been washed out. When the bag is now opened, a sticky material is found in it. This is called *gluten*. The chemist therefore finds that the flour contains starch and gluten. He learns this by **separating** the components.

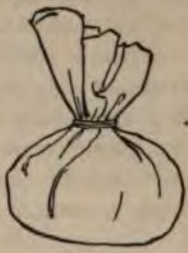

FIG. 4.

Law of Component Substances. — **Every material can be described** as being **composed of one substance,** or as being **a mixture**

---

* Crystals (see also Index) are natural forms, of geometrical outline, which solid substances assume. Usually each substance has a more or less distinct form of its own, the particular angles at which the faces meet being peculiar to the substance. Its individual crystalline form is therefore a specific physical property of each substance.

of two or more component substances, each of which has a definite set of specific physical properties. This is the first and most fundamental law of chemistry. This conception was first clearly stated by Lomonossov (1742), a Russian author, statesman, and chemist (1711–1765).

Mixtures and Impurities. — A material containing more than one component substance is called a **mixture.** The characteristic of a mixture is that **each of the component substances,** although mixed with the others, **possesses exactly the same properties as if it were present alone.** No one of the components affects any other component, or alters any of its properties. Granite and flour are typical mixtures.

When a specimen is composed mainly of one substance, and contains only minute amounts of one or more other substances, it is frequently spoken of as a specimen of the main substance containing certain specified substances as **impurities.** To be called an impurity, the foreign matter need not be dirty or offensive. Thus, common salt usually contains a little magnesium chloride, a white crystalline solid, as an impurity, and it is this impurity which becomes damp in wet weather. Again, compounds of lime and magnesium are common impurities in drinking water.

Components. — The **ingredients of a mixture** are called the **components** (Lat., *put with*), because they are simply placed together, without change, and can be separated without change.

Bodies or Specimens. — It will be seen that *substance* is a general term, like the word "dog," covering the whole species. The *substance* iron includes all the iron in the universe. When we refer to a particular piece of iron, we call it a **body** or a **specimen.** If the body is homogeneous (all parts alike), it may be made of a single substance. If it is heterogeneous (differing in different parts) it is a specimen of a mixture like granite.

The Rusting of Metals. — If we return once more to the subject of rusty iron, we find another point which interests the chemist. If the iron is kept moist — for example, by lying in the grass or partly immersed in water — the layer of rust gradually becomes thicker, and the core of iron becomes thinner, until it finally disappears. The rust seems to be *formed from the iron*, in presence of air and moisture. The iron, particle by particle, loses the properties of iron and simultaneously acquires those of rust. Now **the chemist is concerned,** not only with recognizing substances, but also **with the ways in which substances change and new substances are produced.**

Several other familiar metals rust, as does iron, but the change is slower. Thus, lead rusts (tarnishes) slowly, and zinc still more slowly. The change can be hastened by heating. For example, if some lead is melted in a porcelain crucible (Fig. 5) and is stirred with an iron wire, a dirty yellow powder collects on the surface. Gradually more and more of the powder is formed and less and less of the metallic lead remains, until at last all the metal is gone. Melted tin, when treated in the same way, gives a white powder.

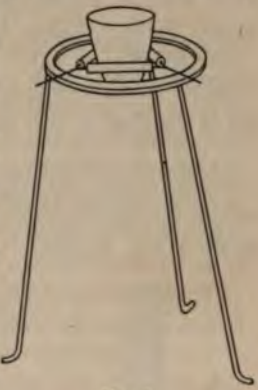

FIG. 5.

Explanation of Rusting. — The first fact which seemed to throw light on the subject was discovered by a French physician, Jean Rey (1630), who found that the rusts of tin and lead, made by heating and stirring, were *heavier* than the original pieces of metal. He inferred, correctly, that the additional material which caused the increase in weight came from the air. He imagined, however, that the rust was not a new substance, but a sort of froth, and therefore a mixture of air with the metal. Other investigators, such as Hooke (1635–1703) and particularly Mayow (1645–1679), in England, explained the increase in weight by supposing that some material from the air had *combined with* the metal. In other words, iron, for example, was one substance composed of iron only, and rust was another substance, made by union of iron and a material from the air, and not a mere mixture.

It was Lomonossov (1756) who first proved by an experiment that the extra material did come from the air. He placed some tin in a flask, sealed up the mouth of the vessel, and weighed the whole. The flask was then heated and the tin was converted into the white powder. So long as the flask remained sealed, no change in weight was found to have occurred. When the mouth of the flask was opened, however, some air rushed in, and the total weight was then found to be greater. Evidently, during the heating, a portion of the original air had forsaken the gaseous condition and joined itself to the tin to form the powder. This left a partial vacuum in the flask, and more air entered when the latter was opened. Eighteen years later the same experiment was made by Lavoisier, who drew the same conclusion. The rusting of other metals was found to be due to the same cause. Lavoisier named the gas, taken from the air, oxygen.

The conclusion can be confirmed in various ways. For example, when the air is pumped out of the flask before it is sealed, the metal can be heated in the vacuum indefinitely without rusting.

Experiment to show the Nature of Rusting. — That a part of the air is consumed when iron rusts is easily proved. We moisten the interior of a test-tube and sprinkle some powdered iron so that it covers and adheres to the whole interior surface. We then set the tube mouth downwards in a dish of water (Fig. 6). At first, the pressure of the water compresses the air in the tube very slightly, and the water ascends above the mouth to the extent of a small fraction of an inch only. As the moist iron slowly rusts, however, the oxygen is gradually removed, and the pressure of the atmosphere outside slowly pushes the water farther up the tube. After an hour or more, the water has ascended about one-fifth of the total distance towards the top of the tube. Evidently part of the air has forsaken the gaseous condition, and the water has been forced up to take its place. Inspection now shows some reddish particles, where rusting has taken place. The rust, then, is made up of a part of the iron and all of the oxygen that the tube contained.

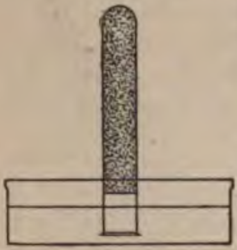

FIG. 6.

Of course, much of the iron powder is still gray, and has not rusted. The air in the tube did not contain oxygen enough to combine with all the iron. The iron that remains is as little able to rust in the remaining gas as in a vacuum.

Incidentally we learn from this experiment that atmospheric air contains about one-fifth (20 per cent) oxygen by volume. The remaining four-fifths is almost all nitrogen (79 per cent), a substance which combines with very few materials, while the balance (1 per cent) is made up of gases which do not enter into combination with any known substance. If lead, tin, or zinc had been heated in an enclosed volume of air, they likewise would have taken out the 20 per cent of oxygen and would have left the other gases.

The Law of Chemical Change. — The three examples of rusting show that specimens of matter can lose their original properties and acquire new ones. Since a substance is "a species of matter, with a constant set of properties," we are compelled to decide that, when a material *changes* its properties, it has, in doing so, become a *new* substance. This consideration calls to our attention the **second** of the fundamental **laws of chemistry,** namely, that **the material forming one or more substances** (such as oxygen and iron), without ceasing to exist, **may be changed into one or more entirely different substances.** Such a change is called a **chemical change,** or **action,** or **interaction,** or **reaction.**

The commoner kinds of chemical actions can be divided, for convenience, into four varieties. We can now define the first of these.

First Variety of Chemical Change: Combination. — In each case of rusting, two substances (a gas and a metal) came together to form a third substance (an earthy powder). Apparently two substances may come together in two different ways. They may form a mixture, in which both substances are present and retain their properties, or they may come together to form a single substance with different properties. When **two (or more) substances unite to form one substance,** the change is called chemical **combination** or **union.** The product is called a **compound substance.**

We are very careful never to speak of a compound substance as a mixture. Rust is not a mixture of iron and oxygen; it shows none of the properties of either. Nor do we call a mixture (like granite) a compound, or the operation of mixing, combination or union. These are technical words, in chemistry and, to avoid confusion, may be used only with due regard to their technical meanings.

Constituents. — As we have seen, we speak of the substances in a mixture as the components. When we wish to refer to the forms of matter which are chemically united in a compound, we call them the **constituents** (Lat., *standing together*) of the compound substance. Thus, iron and oxygen are the constituents of rust.

The chemist **separates** (p. 3) the components of a mixture, for that is all that is necessary. He **liberates** the constituents of a compound, however, because *they* are bound together in chemical combination.

The names given to compounds are usually devised so as to indicate the nature of the constituents. Thus, iron-rust is oxide of iron (or ferric oxide, from Lat. *ferrum*, iron). The yellowish powder from lead is lead oxide or oxide of lead, and the white powder from tin is oxide of tin.

A Condensed Form of Statement. — We may represent a chemical combination, or indeed any kind of chemical change, in a condensed form, thus:

$$\text{Iron} + \text{Oxygen} \rightarrow \text{Oxide of iron (ferric oxide).}$$

Each name stands for a substance. Two substances in contact with one another (mixed), but not united chemically, are connected by the + sign. The arrow shows where the chemical change comes in, and the direction of the change. We read the statement thus: Iron and oxygen brought together under suitable conditions undergo chemical change into oxide of iron, called also ferric oxide. Similarly we may write:

$$\text{Lead} + \text{Oxygen} \rightarrow \text{Oxide of lead.}$$
$$\text{Tin} + \text{Oxygen} \rightarrow \text{Oxide of tin.}$$

The Increase in Weight in Rusting. — As we have seen, the process of rusting is accompanied by a slow increase in the weight of the solid, due to the gradual addition of oxygen to the metal. Now, this increase in weight ceases of its own accord, when a certain maximum has been reached. This occurs when the last particles of the metal have disappeared. Thus, the lead gains in weight until every 100 parts of the metal have gained 7.72 parts of oxygen, and the tin until every 100 parts have gained 26.9 parts of oxygen. When these increases have occurred, the metal is found to have been all used up, and prolonged heating and stirring cause no further union with oxygen and no further change in weight. This fact, that each substance limits itself of its own accord to combining with a fixed proportion of the other substance, in forming a given compound, is one of the most striking facts about chemical combination. In mixtures, any proportions chosen by the experimenter may be used. In chemical union, the experimenter has no choice; the proportions are determined by the substances themselves. Thus, 100 parts of iron when turning into ordinary red rust take up 43 parts of oxygen, no more and no less.

This fact enables us to make our condensed statements more specific and complete by including in them the proportions by weight used in the chemical change:

$$\text{Iron } (100) + \text{Oxygen } (43) \rightarrow \text{Ferric oxide } (143).$$
$$\text{Lead } (100) + \text{Oxygen } (7.72) \rightarrow \text{Oxide of lead } (107.72).$$

The following numbers, which represent the *same proportions* by weight, are the ones commonly used by chemists:

$$\text{Iron } (111.68) + \text{Oxygen } (48) \rightarrow \text{Ferric oxide } (159.68).$$

Summary. — Thus far, we have learned that chemistry deals with substances and their physical properties, and with the changes which substances undergo. We have discussed and defined a number of important words expressing fundamental chemical ideas. Finally, we have touched upon the weights of the materials used in chemical change, a subject of great importance which will be more fully developed in a later chapter.

Exercises. — 1. Take one by one the words or phrases printed in black type and the titles of the sections in this chapter, and endeavor to recollect what you have read about each. In each case try, (*a*) to recall the meaning and to state it in your own words; (*b*) to recall the facts associated with, and the reasoning which lead up to the point in question; (*c*) to recall examples illustrating the conception and to apply the conception in detail to each example. Whenever memory fails to give a perfectly clear report of the matter in hand, the text must be read and re-read until the essential point can be repeated from memory.

Use the same method in all future chapters. A useful practice is to employ a pencil as you read and to underline systematically all the important facts and statements, and then to go back and apply to each marked place the process described above.

2. Define the following terms: Specific gravity, tenacity, melting-point, specific physical property, pure body, vacuum.

3. Is it logical to say "pure substance?"

4. Why do we decide that granite is a mixture and iron a single substance?

5. Do the statements in the text indicate that air is a mixture or a compound?

6. What weight of oxygen would be required to convert 25 grams of lead into oxide of lead?

7. Make a list of the technical words we have defined, and place the definition opposite to each.

8. What weight of tin would be contained in 15 grams of oxide of tin?

9. If any of the following are mixtures, mention the facts which show them to contain more than one substance: (*a*) muddy water, (*b*) an egg, (*c*) milk.

10. In recognizing a specimen to be quartz, does the chemist consider (*a*) the weight, (*b*) the temperature, (*c*) the length of the specimen? If not, why not?

11. Give a list of the specific properties mentioned in this chapter.

CHAPTER II

CHEMICAL CHANGE AND THE METHODS OF STUDYING IT

WE must now take up two new examples of chemical change. They will aid us in introducing one or two additional conceptions and laws. These are continually used by the chemist, and without them we cannot begin the systematic study of the science.

Another Case of Combination: Iron and Sulphur. — Since oxygen is an invisible gas, there is a slight difficulty in realizing that rusting consists in the union of *two* substances — this gas and a metal. The present example is less interesting historically, but it is simpler because both substances are visible and are easily handled. The case of iron and sulphur will enable us to illustrate the same point of view and to practice the application of the same technical words. It will also introduce us to two manipulations — filtration and evaporation — which are frequently used by the chemist.

We begin by observing the physical properties of the two substances. Those of iron have already been noted (pp. 1–2).* Sulphur is a pale-yellow substance of low specific gravity (sp. gr. 2). It is easily melted (m.-p. 112.8° C.). It does not dissolve in water — that is, it does not mix completely with and disappear in water, as sugar does on stirring. It does dissolve readily in carbon disulphide, however. It crystallizes in rhombic forms (Fig. 7). It is not attracted by a magnet.

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* References to previous pages are used in order to save needless repetition in writing. The beginner requires endless repetition in his reading, however, and must *form the habit* of examining, in conjunction with the current text, the parts referred to. The passages cited are, by the reference, *made part of the current text*, which will usually not be clear without them. The same remark applies to topics referred to by name. Such topics must be sought in the index.

All terms, and especially those borrowed from physics, if not perfectly familiar, must be looked up in a work on physics or in a dictionary.

Study of the Mixture, before Combination. — Now, if some iron filings and pulverized sulphur are stirred together in a mortar, the result is a *mixture*. True, the color is not that of either substance, but with a lens particles of both substances can be seen. Passing a magnet over the mixture will easily remove a part of the iron, and with the help of a lens and a needle the mixture can be picked apart particle by particle, completely. We can **separate** the *components* of the mixture more expeditiously, however, **by using** manipulations based upon certain **suitable properties.** Thus, sulphur dissolves in carbon disulphide while iron does not. If, therefore, a part of the mixture is placed in a dry test-tube along with some carbon disulphide (Fig. 8), and is shaken, the liquid dissolves the sulphur and leaves the iron. To complete the separation, the iron must be removed from the liquid by filtration, and the sulphur recovered by evaporation of the carbon disulphide.

FIG. 7.

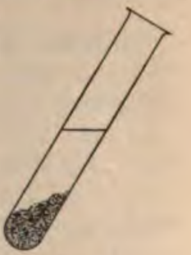

FIG. 8.

Filtration. — Iron, or any solid, when it is mixed with a liquid or with a solution (like the solution of sulphur in carbon disulphide) is said to be **suspended** in the liquid. If the solid is one that settles rapidly, the liquid may be separated from the solid, in a rough way, by pouring off as much of the clear, supernatant liquid as possible. This is called **decantation.**

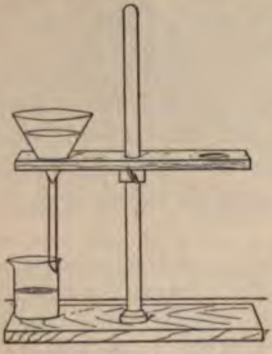

FIG. 9.

A complete separation is effected by pouring the mixture on to a cone of filter paper supported in a glass funnel (Fig. 9). The liquid, together with anything that may be dissolved in it, runs through the pores of the paper and down the hollow stem of the funnel. The liquid is then called the **filtrate.** The particles of the suspended solid are too large to pass through the pores, and so collect on the surface of the filter paper.

This operation, like everything the chemist does, takes advantage of the physical properties of the various materials.

The material remaining on the paper (the **residue**), when dry, is wholly attracted by a magnet and shows all the other properties of iron.

Evaporation. — To recover the sulphur, the solution in carbon disulphide — the filtrate — is poured into a porcelain evaporating dish (Inflammable! Keep flames away). When the vessel is set aside, the liquid gradually passes off in vapor (e-vapor-ates). Sulphur, however, does not evaporate at room temperature and remains as a **residue**, in the form of crystals of rhombic outline in the bottom of the dish (Fig. 10). Here, again, physical properties have been utilized.

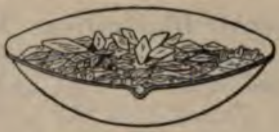
FIG. 10.

Since the physical properties of two substances are not changed by mixing, we have thus used the properties of the iron and sulphur so as to separate them once more. The iron is on the paper; the sulphur is in the dish.

Combination of Iron and Sulphur. — But iron and sulphur are capable of combining. If we alter the conditions by raising the temperature of some of the dry mixture, as we did in causing lead to rust rapidly, chemical union sets in. When we place some of the original mixture of iron and sulphur into a clean test-tube and warm it, we soon notice a rather violent development of heat taking place, the contents begin to glow, and what appears to be a form of combustion spreads through the mass. The heating employed at the start falls far short of accounting for the much greater heat produced. When these phenomena have ceased, and the test-tube has been allowed to cool, we find that it now contains a somewhat porous-looking, black solid. This material is brittle; it is not magnetic; it does not dissolve in carbon disulphide; and close examination, even under a microscope, does not reveal the presence of different kinds of matter. This substance is known to chemists as ferrous sulphide and, as we see, its properties are entirely different from those of its constituents.

In this connection we must not omit to notice that, as in rusting, a certain fixed proportion will be used in forming the compound. We find that, for 7 parts of iron, almost exactly 4 parts by weight of sulphur are required. If more iron is put into the original mixture, then some unused iron will be found in the mass after the action. If too much sulphur is employed, some may be driven off as vapor by the heat and any that remains, beyond the correct proportion, can be dissolved out of the ferrous sulphide with carbon disulphide. The sulphur which has combined with the iron, however, is no longer present as sulphur — it has no longer the properties of sulphur, and therefore cannot be dissolved out:

Iron (55.84) + Sulphur (32.07) → Ferrous sulphide (87.91).

Another Illustration: Mercuric Oxide. — It has long been known that air contains an active and an inactive gas. The Chinese called them *yin* and *yang*, respectively. Mayow (1643–1679) showed that the active gas caused rusting, that it was absorbed by paint (really by the linseed oil) in "drying," that it supported combustion of wood and sulphur, and that it is necessary to life, being absorbed by the blood from the air entering the lungs. It was not until 1774, however, that a pure specimen of this gas was obtained, by Priestley, and was recognized to be a special kind of gas different from ordinary air. The gas (later to be named oxygen) was made by Priestley from mercuric oxide, a bright red, rather heavy powder. When the oxide is heated (Fig. 11), we find that a gas is given off. This gas is easily shown to be different from air, since a glowing splinter of wood is instantly relighted on being immersed in it. The gas is pure oxygen. During the heating, we notice also that a metallic coating appears on the sides of the tube, in the form of a sort of mirror. Apparently the vapor of some metal is coming off with the oxygen and condensing on the cool parts of the tube. As this shining substance accumulates it takes the form of globules, which may be scraped together. It is, in fact, the metal mercury, or quicksilver. If the heating continues long enough, the whole of the red powder eventually disappears, and is converted into these two products.

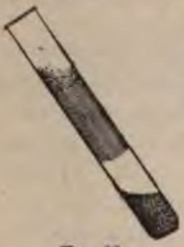

FIG. 11.

Second Variety of Chemical Change: Decomposition. — Priestley's experiment introduces to us a second, and very common kind of chemical action. The first variety was combination or union (p. 7). The **second** is called **decomposition.** It consists in starting with **a single substance** (here mercuric oxide) and **splitting it into two** (**or more**) **substances,** which differ in properties from the substance taken and from one another. Here, the red powder gave mercury, a liquid metal, and oxygen, a colorless gas.

Simple and Compound Substances. — We have seen that two (or more) substances, like lead and oxygen, can combine to form a compound substance. Are all substances, then, compounds? We find that some are not. We have never succeeded in obtaining lead, or oxygen, or iron, or tin, or sulphur by combining any two substances. We can decompose mercuric oxide by heat, and we have other ways of decomposing compounds like oxide of tin and ferrous sulphide, but we have never succeeded in decomposing the mercury or the oxygen, the iron or the sulphur themselves. **Substances which we are not able, at will, to decompose into, or to make by chemical union from, other substances** are called **simple or elementary substances.** The distinction between simple and compound substances was first drawn by Lomonossov in 1741. Later, and independently, it was stated very clearly by Lavoisier (1789).

Several substances, regarded in Lavoisier's time as elementary, have since been shown to be compounds. Thus, quicklime was a simple substance until Davy, in 1808, prepared the metal calcium and showed that quicklime was the oxide of this metal. Hence, we do not say that the substances regarded as simple *cannot* be decomposed, but only that they are substances which we "are not able" (at present) to decompose.

The phrase "at will" is also important. Radium (*q.v.**) cannot be decomposed at will, but it undergoes continuous "disintegration," producing the elements helium and lead. We can neither hasten, retard, nor stop this spontaneous decomposition.

The highly interesting experiments of Collie, Paterson, and Masson (Chemical Society, London, *Annual Report*, 1914, pp. 41–47) seem to show that the elements helium and neon can be produced by electrical discharges in vacuum tubes and even in a closed tube surrounding the vacuum tube. Before long, therefore, the decomposition of elementary substances, and the formation of some elements from others, *at will*, may be a recognized possibility, and the foregoing definition may have to be radically revised.

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* Contraction for *quod vide*, which see. This abbreviation is used when subjects not yet discussed are mentioned. For such subjects, consult the index.

Elements. — The word element is used in two senses. It is applied to the simple substance. Thus we speak of "the element iron," meaning the metal iron. It is applied also to the iron-matter contained in ferrous sulphide or in ferric oxide. The reader should note that it is correct usage to speak of the *element* iron and the *element* sulphur in ferrous sulphide, but a chemist would never say that this compound contained the *simple substances* iron and sulphur. If he did, we should understand him to mean that it was a mixture, and we should expect parts of the material to be magnetic like iron, and other parts to be yellow and soluble in carbon disulphide, which is not the case. In the same way the *name* of an element (such as iron) is applied both to the material in combination and to the free substance. Thus "iron" may mean free, uncombined, metallic iron, or iron-matter in some compound. The sense in which the word is employed must be inferred from the context or circumstances. When a chemist speaks, as he sometimes does, colloquially, of "iron" in a drinking water, for example, we know at once that he refers to iron in the form of some compound, for metallic iron does not dissolve in water and, if it did, would quickly turn into rust or some other form of combination.

The word **element,** then, means **one of the simple forms of matter, either free or in combination.**

In formally describing a body or specimen, the chemist always avoids the ambiguity just referred to *by naming the components*, *i.e.*, the substance or substances it contains. He assumes that the nature and constituents of these substances will be known to anyone hearing or reading the description. If he says the body contains zinc and sulphur, it is understood that the body is a mixture of these simple substances. If it contained these elements in combination, the chemist would report that it was sulphide of zinc.

The Common Elements. — Thousands of different compound substances are known but, when they are decomposed, it is found that the number of different *elements* contained in them is not great. Dozens of substances contain iron, hundreds contain sulphur, thousands contain oxygen. In fact, by combining a limited number of simple substances, two, three, or four, together, in varying proportions by weight, an almost unlimited number of different compound substances could be produced.

A list of the elements appears on the inside of the cover, at the end of this book, and contains about eighty names. Of these, a large number are rare, and seldom encountered. More than 99 per cent of terrestrial material is made up of eighteen or twenty elements and their compounds. Only about twenty elements occur in nature in their simple, uncombined condition. Three-fourths of the whole number are found in combination exclusively, and must be liberated by some chemical action.

Taking the atmosphere, all terrestrial waters, and the earth's crust, so far as it has been examined, F. W. Clarke has estimated the plentifulness of the various elements. The first twelve, with the quantity of each contained in one hundred parts of terrestrial matter, and constituting together 99 per cent, are as follows:

Oxygen	49.85	Calcium	3.18	Hydrogen	0.97
Silicon	26.03	Sodium	2.33	Titanium	0.41
Aluminium	7.28	Potassium	2.33	Chlorine	0.20
Iron	4.12	Magnesium	2.11	Carbon	0.19

Thus oxygen accounts for nearly one-half of the whole mass. Silicon, the oxide of which when pure is quartz and in less pure form constitutes ordinary sand, makes up half of the remainder. Valuable and useful elements, like gold, silver, sulphur, and mercury, are among the less plentiful which, all taken together, furnish the remaining one per cent.

Law of Definite Proportions. — In the decomposition of mercuric oxide (p. 14) we find that, for every 100 parts of mercury liberated, almost 8 parts of oxygen (more exactly, 7.97 parts) by weight are set free. Using the numbers commonly employed in chemistry, which represent the same proportion by weight:

Mercuric oxide (216.6) → Mercury (200.6) + Oxygen (16).

We find also that mercury and oxygen can be made to combine to form mercuric oxide, and the proportions by weight required are the same. Moreover, every sample of mercuric oxide, whether made by combination, or in any of the other possible ways, always contains this proportion of the two elements. We have already seen that the oxides of lead and tin contain fixed proportions (p. 9) of the metal and oxygen and that ferrous sulphide has a constant composition by weight. The same principle is found to apply to all chemical compounds, and is stated in the **law of definite or constant proportions: In every sample of any compound substance, formed or decomposed, the proportion by weight of the constituent elements is always the same.** (For the only known exception to this law, see radium.)

Conservation of Mass. — The most painstaking chemical work seems to show that, if all the substances concerned in a chemical change are weighed before and after the change, there is no evidence of any alteration in the *quantity of matter*. The two weights, representing the sums of the constituents and of the products, respectively, are, indeed, never absolutely identical, but the more careful the work and the more delicate the instrument used in weighing, the more nearly do the values approach identity. We are able to state, therefore, that **the mass of a system is not affected by any chemical change within the system.**

This statement simply means that the great law of the conservation of mass holds true in chemistry as it does in physics. Chemical changes, thoroughgoing as they are in respect to all other qualities, do not affect the mass; an element carries with it its weight, entirely unchanged, through the most complicated chemical transformations.

Superficial observation, as of a growing tree, might seem to give evidence of the very opposite of conservation of matter. But here the carbon dioxide gas in the air, the most important source of nourishment for plants, is overlooked. Similarly, the gradual disappearance of a candle by combustion seems to illustrate the destruction of matter. But if we catch *the gases* which rise through the flame (Fig. 12), we find that the gases weigh even more than the part of the candle which has been sacrificed in making them. When we take account of the weight of the oxygen obtained from the air which sustains the combustion, we find that there is really neither loss nor gain in weight. If we carry out chemical changes in closed vessels (Fig. 13), which permit neither escape nor access of material, we find that the weight does not alter.

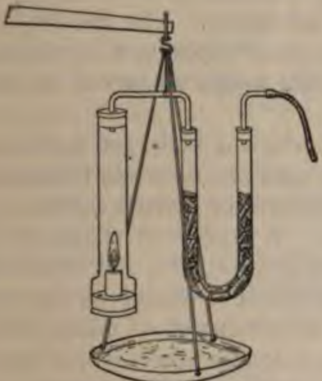

FIG. 12.

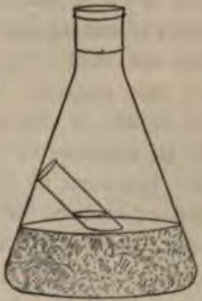

FIG. 13.

Specific Physical Properties. — It will be seen that, to the chemist, knowing the physical properties of all substances is very important. By means of the properties, he recognizes and describes all the bodies he studies. It may be well, therefore, here to give a list of the more important properties, most of which have been mentioned in connection with the illustrations we have used.

In the case of **solids**, the chief physical properties the chemist uses are **color**, **crystalline form**, **solubility** or non-solubility in water and occasionally other liquids, the temperature at which the substance melts (**melting-point**), and the **density**.

In the case of **liquids**, he notes the temperature at which the liquid boils (**boiling-point**), the **density**, the **mobility**, the **odor**, and the **color**.

Finally, in the case of **gases**, the properties commonly mentioned are the **color**, **taste**, and **odor**, the **density**, **solubility** in water, and the ease or difficulty with which the gas can be **liquefied**.

Attributes and Conditions. — There are other qualities which a body may possess that we are liable to confuse with the specific properties. Thus, the weight of a piece of sulphur is not a property of sulphur. A hundred pieces of as many different substances might all have the same weight, so that a particular weight (say 2 grams) is not a property of any one species of matter. **Weight, dimensions,** and **volume** are **attributes** of a **body.** They have different values for different bodies, even when those bodies are all composed of the same substance. The attributes are physical in nature. They are of great importance in chemistry, however, because **they afford the only means we have of measuring quantities of substances.**

There are still other qualities which a body (or specimen of matter) may possess. It has, for example, a certain **temperature, pressure** (state of compression), **motion,** or **electric charge,** and it may be **in solution** in some liquid. A body may change in temperature, pressure, or state of electrification, or it may be dissolved in water, or be recovered by evaporation of the liquid, and yet be the same specimen. A hundred specimens of as many different substances may all have the same temperature — this is not a specific property. These are all spoken of as **conditions.** They are physical conditions. In chemistry, conditions are often altered in order to bring about, or to stop chemical change, or to modify the speed with which it takes place. Thus, we heated the lead (raised its *temperature*) in order to hasten the process of rusting. If a substance, or mixture, is capable of undergoing ordinary chemical change, then the change is always hastened by raising the temperature, and is always delayed or prevented by lowering the temperature. Similarly, changing the pressure in a gas, or dissolving a substance in some liquid, frequently hastens or delays a chemical change in which the substance takes part. The proper physical conditions are, therefore, considered in connection with every chemical operation. **Conditions are used to modify chemical change.**

Physics in Chemistry. — It will be seen that one cannot accomplish anything in chemistry without acquiring and using some knowledge of physics. We measure quantities by means of the physical attributes, weight and volume. We produce chemical change by arranging the physical conditions, for example, by mixing, heating, or using an electric current. Physical means are the only means we possess for producing, stopping, or modifying chemical changes. Again, we ascertain whether a chemical change has taken place or not by observing the physical properties of the materials before and after the experiment. Thus, we noted that the red, powdery oxide of mercury, when heated, gave a liquid metal and a gas. All the phenomena of chemistry are physical. A phenomenon is literally something that is *seen* or, more generally, something that affects any of the senses. Observing physical phenomena is, therefore, our sole means of studying chemical changes. Chemical work is, in fact, entirely dependent upon the skilful use of physical agencies, and upon the close observation of physical phenomena for its success.

It is only the inference, following the experiment and the observation, that is strictly chemical. If one substance gives two different substances, or if two substances give one different substance, for example, we infer that a chemical change has occurred. We then try to recognize the substances by their properties and name them.

Changes like that of ice into water, or of water into steam, and *vice versa*, are not regarded as chemical changes. These are called **changes of state,** or of state of aggregation. The solid, liquid, and gaseous forms are different states of the same substance.

Law: Explanation: Scientific Method. — There is a widely spread impression that a *science*, like chemistry, is a part of the natural order of the universe. It is thought that we are trying to find the boundaries of chemistry, as they have been predetermined by nature, and to discover the facts, relations of facts, and laws which nature has provided as a means of classifying the content of the science. Now, the situation is precisely the reverse of this. Nature provides only the materials and the phenomena, and *man* is attempting to classify them. He divides the whole into groups, such as physics, chemistry, botany, etc. Then he classifies the facts within each group, in order that he may more easily remember them and perceive their relations. He often finds that, when new facts are discovered, parts of the classification have to be changed. Thus, as we have just seen, changes of state are usually assigned to physics, but Ostwald at one time suggested that they should be considered as chemical phenomena.

In the preceding pages, we have discussed some of the ways that have been invented for classifying the materials and facts assigned to chemistry. Thus, we pick out a number of facts of a like nature and try to make a single statement which will cover all these facts. For example, we find about one hundred thousand different substances and, in the case of *each substance, every specimen* that we have examined contains the same proportions of the constituent elements. So we formulate the law of constant proportions. A **law** or **generalization** in chemistry is **a brief statement describing some general fact or constant mode of behavior.** We must remember, however, that **laws are only true so long as no facts in conflict with them are known.** There are no laws in nature. Nature presents materials and phenomena as she pleases. The laws are parts of *science*, which is *made by man*, and is a description of natural facts as man knows them. As we have seen (p. 18), at least one undoubted exception to the law of constant proportions has recently (1914) been discovered, and other exceptions to this law will undoubtedly present themselves.

One section (p. 5) was entitled: "**Explanation** of rusting." If that paragraph be now re-read, it will be found that, in the ordinary (as distinct from the scientific) sense of the word, no explanation was given! When we ask a man to "explain" some feature in his conduct, we recognize that he might have chosen to act otherwise, and we wish to know *why* he acted precisely as he did. Nature, however, has no free will, and cannot tell why she presents certain phenomena, and not others.

On examining the explanation, we find that it simply shows that when iron rusts it combines with oxygen from the air. This is an additional fact. It shows *how* iron rusts, namely by taking up oxygen, but not *why* it is able to unite with oxygen. We simply do not know why iron can combine with oxygen gas and platinum cannot.

Explanations in chemistry are of three kinds. (1) We usually try to show that the phenomenon is not an isolated one. Thus, we show that other metals rust. This reconciles us to some extent to the fact that iron rusts, and we feel some mental satisfaction. This is the method of **showing that the fact to be explained is a member of a large class of similar facts.** (2) Next, **we try to get more information about the fact to be explained.** Thus, when, to the acquaintance with the outward manifestations of rusting, we add the further information that there is an increase in weight, and that this is due to union of oxygen from the air with the iron, we feel increased satisfaction, and say that the fact has been "explained." (3) If we are still dissatisfied, and can discover no further useful facts, **we imagine a state of affairs which, if true, would classify the fact or add to what we know about it.** This step we call explaining by means of an **hypothesis.** We then devote our attention to trying to verify the hypothesis.

The formulation of laws and the making of attempts to explain facts are part of what is called the **scientific method.** The purpose of this method is to convert the subject matter into **a science,** that is, into **an organized body of knowledge.**

Summary. — In this chapter we have learned: (1) that, while there are many substances, there is a limited number of entirely different kinds of matter (elements); (2) that, in addition to constant physical properties, each substance has a constant composition by weight. We have also learned that physical properties are utilized in manipulations, like filtration and evaporation, as well as for identifying substances, and that physical attributes are used for measuring quantities in chemistry and physical conditions for guiding chemical change. Finally, we have seen that a science is not a natural, but a manufactured product, and that the science of chemistry is still in the making.

*Exercises.** — 1. What physical properties are used (*a*) in filtration, (*b*) in evaporation, (*c*) in the separation and identification of the products from heating mercuric oxide (p. 14)?

2. Describe: (*a*) a red-hot rod of iron, 10 cm. long by 1 cm. diameter, weighing 58.5 g.; (*b*) a solution of 5 g. of sulphur in 20 c.c. (59 g.) of carbon disulphide at 18° C. In doing so, divide the description into attributes, conditions, and properties.

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* The exercises should in all cases be studied with minute care. They not only serve as tests to show that the chapter has been understood, but very frequently (as in No. 4) also call attention to ideas which might not be acquired from the text alone, or (as in Nos. 1, 2, 5) assist in elucidating ideas given in the text which, without the exercises, might not be fully grasped.

connection between it and the air! Bayen (Apr., 1774) was the first to make it by heating mercuric oxide. Priestley (Aug. 1, 1774) made it by heating the same substance and quite purposelessly, as he admits, thrust a lighted candle into it and was delighted with the extreme brilliance of the flame. He had, however, entirely incorrect ideas about its nature, and no notion until a year later that it was a component of the air. Scheele, a Swedish apothecary, had made it in 1771–2 from no less than seven different substances and understood clearly that atmospheric oxygen combined with metals, phosphorus, hydrogen, linseed oil and many other substances. But the publisher did not get his book out until 1777, and Priestley is usually credited with the "discovery" of the element. Finally, Lavoisier (1777) heated mercury in a retort (Fig. 14), the neck of which projected into a jar standing in a larger dish of mercury. The air, thus enclosed within the jar and the retort, during twelve days lost one-fifth of its volume. Simultaneously, red particles of mercuric oxide accumulated on the surface of the mercury in the retort. The residual gas, nitrogen, no longer supported life or combustion. The oxide, on being heated more strongly, by itself, gave off a gas whose volume exactly corresponded with the shrinkage undergone by the enclosed air, and this gas possessed in an exaggerated degree the properties which the air had lost. The proof that oxygen was a component of the atmosphere was therefore complete. Later, Lavoisier, in the mistaken belief that the new element was an essential constituent of all sour substances, named it **oxygen** (Gk., *acid-producer*).

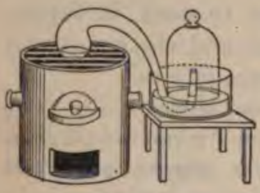

FIG. 14.

Occurrence. — As we have seen, nearly 50 per cent of terrestrial matter is oxygen. Water contains about 89 per cent, the human body over 60 per cent, and common materials like sandstone, limestone, brick, and mortar more than 50 per cent of this element. One-fifth by volume (nearly one-fourth by weight) of the air is free oxygen.

Preparation of Oxygen. — 1. The oxygen of commerce is now made chiefly from **liquefied air** (*q.v.**). The liquid oxygen boils at −182.4°, but the nitrogen boils at an even lower temperature (−194°). Since the liquid air has a temperature of about −190°, somewhat above that of boiling nitrogen, the latter evaporates much more freely than does the oxygen. After a time, when the remaining liquid is almost pure oxygen (96 per cent), the gas coming off is compressed by pumps into the steel cylinders (Fig. 15) in which it is sold. In medicine, patients suffering from pneumonia or suffocation obtain some relief by inhaling it in this form. It is also used in feeding flames, instead of air, when intense heat is required (see acetylene torch and calcium light).

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* See p. 15, footnote.

2. Unfortunately, it is difficult to liberate oxygen from **natural substances.** Saltpeter (potassium nitrate), for example, which is found in many soils and can be dissolved out with water, gives off oxygen (p. 25) only when raised to a bright red heat by the Bunsen flame or blast lamp. But it gives up only one-third of the oxygen it contains (101.1 g. give 16 g. of oxygen).

3. In practice, we are compelled to use manufactured substances. Amongst the artificial substances are mercuric oxide, expensive but historically interesting (p. 14), potassium chlorate, perhaps the most convenient for laboratory use, and sodium peroxide.

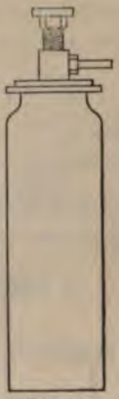

Fig. 15.

Potassium Chlorate (*q.v.*) is a white crystalline substance used, on account of the oxygen it contains, in large quantities in the manufacture of matches and fireworks. When heated in a tube similar to that in Fig. 11, it first melts (351°) and then, on being more strongly heated, it effervesces and gives off a very large volume of oxygen. Examination shows that the whole of the oxygen it contains (39 per cent) can be driven out. The white material which remains after the heating is identical with the mineral sylvite. To the chemist it is known as potassium chloride. The change, together with the weights of the materials, is as follows:

Potassium chlorate (122.56) → Potassium chloride (74.56) + Oxygen (48)

Potassium (39.1)	Potassium (39.1)
Chlorine (35.46)	Chlorine (35.46)
Oxygen (48)	

A peculiarity of this action is that admixture of manganese dioxide (the mineral pyrolusite) increases very markedly the speed with which the decomposition of the potassium chlorate takes place. Hence, in its presence, and it is generally mixed with the chlorate in laboratory experiments (Fig. 16), a sufficient stream of the gas is obtained at a relatively low temperature (below 200°, see p. 29). Hales (p. 25) was the first to collect a gas over water (Fig. 16), in order that it might be kept unmixed with air.

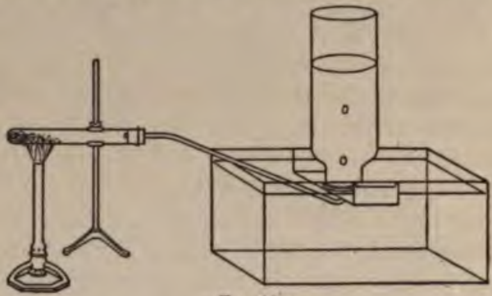

FIG. 16.

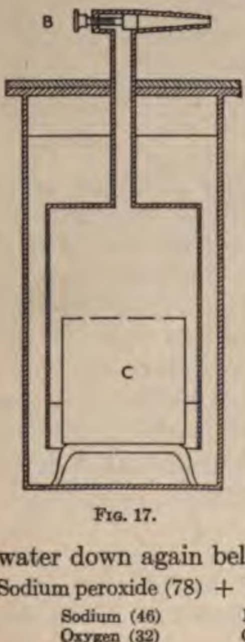

FIG. 17.

4. Oxygen can be obtained conveniently from **sodium peroxide** and water by means of generators (Fig. 17) similar to the acetylene generators used on automobiles. When the metal sodium is burned in air, sodium peroxide is obtained as a powder. This powder, after being melted, solidifies in compact, solid form, and is sold as **oxone.** The oxone is bought in a small, sealed tin can, the ends of which are perforated in several places just before use. When the valve (*B*) is opened, so that the oxygen escapes, the water, which fills the generator almost to the top, enters the can (*C*) by the holes in the bottom and interacts with the oxone. When the valve is shut, the gas continues to be generated until it has driven the water down again below the level of the bottom of the can.

Sodium peroxide (78) +	Water (18) →	Sodium hydroxide (80) +	Oxygen (16)
Sodium (46) Oxygen (32)	Hydrogen (2.016) Oxygen (16)	Sodium (46) Oxygen (32) Hydrogen (2.016)	

This method is convenient because it works at room temperature and can be started and stopped at will. The sodium hydroxide produced is very soluble in water and remains dissolved. Note that the name of this substance indicates the elements which compose it.

Catalytic or Contact Action. — The influence of manganese dioxide in causing the potassium chlorate to decompose more easily (p. 27) well deserves notice. The effect is very striking if some pure potassium chlorate is melted carefully, to avoid superheating, in a wide-mouth flask (Fig. 18). The flask is provided with a wide exit tube, from which a rubber tube may lead to a bottle inverted in a trough filled with water as in Fig. 16. A little manganese dioxide is contained in the upper, closed tube. No effervescence of the chlorate can be seen at its melting-point (334°) — only a little air, expanded by the heating, issues from the tube. When, however, the closed tube containing the manganese dioxide is rotated into a vertical position (see dotted lines), and the black powder falls into the chlorate, the oxygen comes off in torrents, in consequence of the enormous acceleration of the decomposition. As a precaution against injury from an explosion, it is advisable to wrap the flask in a towel before turning the tube.

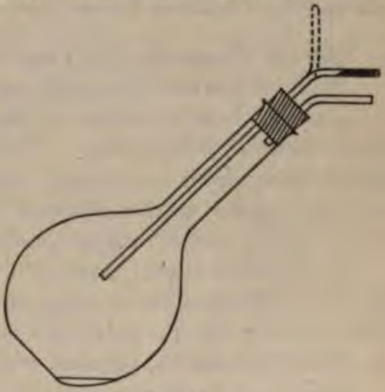

Fig. 18.

It must also be noted that the manganese dioxide is not itself permanently altered. If the material left after the action is shaken with water, the potassium chloride dissolves, while the dioxide does not. Filtration (p. 12) then enables us to recover the latter, and to ascertain that it has been changed neither in quantity nor in properties.

The only effect of the dioxide is to *hasten* the decomposition of the chlorate, which would otherwise be too slow at 200° (p. 28), or even at 334° (its m.-p.) to be of any practical value. **Substances which hasten a chemical action without themselves under-**

going any permanent change are called **contact agents, catalytic agents,** or **catalysts.** The process is called **contact action** or **catalysis** (Gk., *decomposition*, not a very fortunate choice of words). Such substances are frequently used in chemistry. The addition of a suitable catalyst is one of the *conditions* (p. 20) for carrying out actions in which a contact agent is necessary. Many substances of this class are secreted by animals and plants and play an important part in digestion, fermentation, and other physiological changes. Their presence often enables very complex chemical actions to proceed rapidly at rather low temperatures.

The oxone, mentioned above, always contains a trace of cuprous oxide which hastens the action on water.

Specific Properties of Two Kinds, Physical and Chemical. — We have learned that every substance has its own set of specific properties. In describing a substance, it is convenient to divide the properties into two classes. The list of substances with which the given substance can enter into chemical combination, for example, we place under **specific chemical properties.** Relations of the substance to any of the varieties of chemical change belong to this class.

On the other hand, we do not consider melting or boiling to be chemical changes, so we place the temperatures at which the substance melts (m.-p.) and boils (b.-p.), its color, etc. (for list, see p. 19), under **specific physical properties.**

Properties of either class may be used for recognizing a substance.

Specific Physical Properties of Oxygen. — Oxygen resembles air in having neither *color*, *taste*, nor *odor*. The *density* of a substance is, strictly speaking, the weight of 1 cubic centimeter (1 c.c.). In the case of a gas, we frequently prefer to give the weight of 1000 c.c. (1 liter), at 0° and 760 mm. (1 atmosphere) barometric pressure. For oxygen this weight is 1.42900 grams (Morley). The corresponding weight for air is 1.293, so that oxygen is slightly heavier, bulk for bulk, than air (in the ratio 1.105 : 1). Oxygen can be *liquefied* by compression, provided its temperature is first reduced below $-118°$, which is its critical temperature.* The gas is slightly *soluble* in *water*, the solubility at 0° being 4 volumes of gas in 100 volumes of water (at 20°, 3 : 100).

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* Each gas has an individual critical temperature (*q.v.*) above which no pressure, however great, will produce liquefaction. The farther the temperature of a specimen of the gas is below the critical point, the less will be the pressure required to liquefy it.

The solubility of oxygen in water, although slight, is in some respects its most important physical property. Fish obtain oxygen for their blood from that *dissolved in* the water. With air-breathing animals (like man), the oxygen could not be taken into the system, if it did not first dissolve in the moisture contained in the walls of the air sacs of the lungs, and then pass inwards in a dissolved state to the blood.

Liquid oxygen, first prepared by Wroblevski, has a pale-blue color. At one atmosphere pressure, that is, in an open vessel, it boils at −182.5°. Its density (weight of 1 c.c.) is 1.13, so that it is slightly denser than water. By cooling with a jet of liquid hydrogen, Dewar froze the liquid to a snow-like, pale-blue solid. A tube of liquid oxygen is noticeably attracted by a magnet.

Six Specific Physical Properties of Each Gas. — Although every substance has many physical properties, we shall mention only those which are used in chemical work, with occasionally the addition of any peculiar or unexpected quality. It will aid the memory to recall the physical properties of a *gas*, if we note that, as a rule, only *six* such properties are mentioned: (1) color, (2) taste, (3) odor, (4) density, (5) liquefiability, defined by the critical temperature, (6) solubility, usually in water only.

Specific Chemical Properties of Oxygen. — The chemical properties of pure oxygen are like those of atmospheric air, only more pronounced.

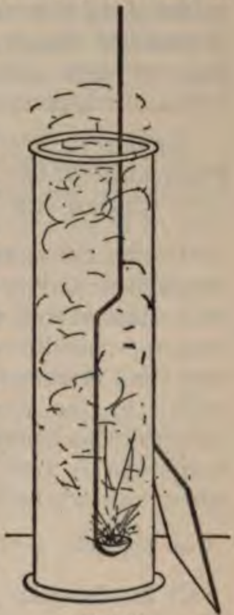

FIG. 19.

Non-metallic Elements. Sulphur, when raised in advance to the temperature necessary to start the action, unites vigorously with oxygen (Fig. 19), giving out much heat and producing a familiar gas having a pungent odor (sulphur dioxide). This odor is frequently spoken of as the "smell of sulphur," but in reality sulphur itself has no odor, and neither has oxygen. The odor is a property of the compound of the two. The mode of experimentation can be changed and the oxygen led into sulphur vapor through a tube. The oxygen then appears to burn with a bright flame, giving the same product as before.

Phosphorus, when set on fire, blazes in oxygen very vigorously, forming a white, powdery, solid oxide — phosphorus pentoxide. Burning carbon, in the form of charcoal or hard coal, glows brilliantly and is soon burnt up. It leaves an invisible, odorless gas — carbon dioxide. At high temperatures, oxygen combines readily with one or two other non-metals (*e.g.*, silicon, boron, and arsenic), and to a small extent (1 per cent at 1900°) with nitrogen. It will not combine directly with chlorine, bromine, or iodine, although oxides of the first and last can be prepared by using other varieties of chemical change. With the six members of the helium family (*q.v.*), of which no compounds are known, and with fluorine, oxygen forms no compounds.

$$\text{Sulphur } (32.06) + \text{Oxygen } (32) \rightarrow \text{Sulphur dioxide } (64.06).$$
$$\text{Phosphorus } (62.08) + \text{Oxygen } (80) \rightarrow \text{Phosphorus pentoxide } (142.08).$$
$$\text{Carbon } (12) + \text{Oxygen } (32) \rightarrow \text{Carbon dioxide } (44).$$

Metallic Elements. Iron, as we have seen, rusts exceedingly slowly in air and, even when red-hot, gives hammer-scale, the black solid which is broken off on the anvil, rather deliberately. In pure oxygen, a bundle of picture-wire, if once ignited, will burn with surprising brilliancy, throwing off sparkling globules of the oxide, melted by the heat. This oxide is a black, brittle substance, identical with hammer-scale, and different from rust (ferric oxide). It contains, in fact, a smaller proportion of oxygen than does the latter, and is called magnetic oxide of iron.

$$\text{Iron } (167.52) + \text{Oxygen } (64) \rightarrow \text{Magnetic oxide of iron } (231.52).$$

All the familiar metals, excepting gold, silver, and platinum, when heated, combine with oxygen, some more vigorously, others less vigorously than does iron. Oxides of the three metals just named can also be made, but only by varieties of chemical change other than direct combination.

Compound substances, if they are composed largely or entirely of elements which combine with oxygen, are able themselves to interact with oxygen. Usually, they produce a mixture of the same oxides which each element, separately, would give. Hence, wood, which is composed of carbon and hydrogen with some oxygen, when burnt in oxygen, produces carbon dioxide and water (oxide of hydrogen) in the form of vapor. Again, carbon disulphide burns readily, giving carbon dioxide and sulphur dioxide, just as do carbon and sulphur, separately. Ferrous sulphide gives, similarly, sulphur dioxide and magnetic oxide of iron.

Tests. A Test for Oxygen. — A **test** is a **property which,** because it is easily recognized (a strong color, for example), or for some other sufficient reason, **is commonly employed in recognizing a substance.**

Oxygen, as we have seen (p. 14), *when pure,* is recognized by the fact that a splinter of wood, glowing at one end, bursts into flame when introduced into the gas. Only one other gas (see nitrous oxide) behaves similarly.

The Measurement of Combining Proportions. — In a number of condensed statements we have given the proportions by weight of the materials combining. It is now desirable that we should know how the necessary measurements are made. The most *exact* measurement of the proportions in which the elements combine to form compounds involves manipulations too elaborate to be gone into here. One or two brief statements, diagrammatic rather than accurate, will show the principles, however.

If we take a weighed quantity of iron in a test-tube and heat it with more than enough sulphur (an **excess** of sulphur), we get free sulphur along with the ferrous sulphide (pp. 13–14), and no free iron survives. We may remove the free sulphur by washing the solid with carbon disulphide. The difference between the weights of the ferrous sulphide and the iron gives the amount of sulphur combined with the known quantity of the latter.

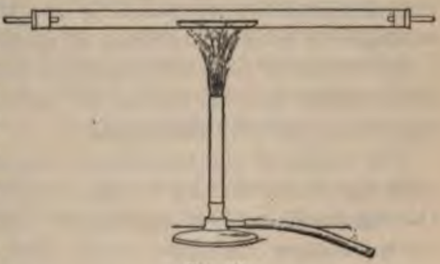

Fig. 20.

As an example of the study of the combination of a metal with oxygen, we may weigh a small amount of copper in the form of powder in a porcelain boat and pass oxygen over the heated metal (Fig. 20). If we limit the oxygen, part of the copper may remain unaltered; if we use it freely, the excess will pass on unchanged. The original weight of the copper, and the increase in weight, representing oxygen, give us the data for determining the composition of cupric oxide. The data furnished by one rough lecture-experiment, for example, were as follows:

Weight of boat + copper	4.278 g.
Weight of boat empty	3.428 g.
Difference = **weight of copper**	**0.850** g.
Weight after addition of oxygen	4.488 g.
Weight without oxygen	4.278 g.
Difference = **weight of oxygen**	**0.210** g.

The proportion of copper to oxygen, so far as this one measurement goes, is therefore 85 : 21.

The results of quantitative experiments are often recorded in the form of parts in one hundred. To find the percentage of each constituent, we observe that the proportion of copper is 85 : 85 + 21, or $\frac{85}{106}$ of the whole. That of the oxygen is $\frac{21}{106}$ of the whole. Thus the percentages are:

$$\text{Copper, } 106 : 85 :: 100 : x. \qquad x = 80.2.$$
$$\text{Oxygen, } 106 : 21 :: 100 : x'. \qquad x' = 19.8.$$

Naturally, the mean of the results of a number of more carefully managed experiments will be nearer the true proportion. The percentages at present accepted as most accurate are 79.9 and 20.1.

In the case of mercuric oxide, we may decompose a known weight of the oxide (p. 14), collect the mercury and weigh it, and ascertain the oxygen by difference.

The names of the constituent elements in a compound, together with the proportion by weight in which they are present, are called the **composition** of the substance. Thus, the *composition* of cupric oxide is copper : oxygen : : 79.9 : 20.1. This is the *percentage* composition, but other numbers expressing the same proportion (such as 63.57 : 16) will serve the purpose.

All **experiments involving measurement,** such as those used in determining composition, are called **quantitative experiments.**

Another Quantitative Experiment. — The following will show how the combining proportions may be measured when the product is a gas, the weight of which must be ascertained. Sulphur burns in oxygen to form sulphur dioxide. A known weight of sulphur is placed in a porcelain boat (Fig. 21), which has already been weighed. The U-shaped tube to the right contains a solution of potassium hydroxide, which is capable of absorbing the resulting gas. The oxygen enters from the left. When the sulphur is heated, it burns in the oxygen, and the loss in weight which the boat undergoes shows the amount of sulphur consumed. The gain in weight of the U-tube shows the weight of the compound produced. By subtracting, we get the quantity of oxygen.

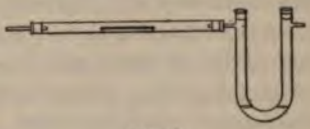

FIG. 21.

In one experiment, the loss in weight of the boat and its contents (= sulphur) was 1.21 g. The weight gained by the U-tube was 2.42 g. The difference (= oxygen) is 1.21. The proportion of sulphur to oxygen in sulphur dioxide is therefore 1.21 : 1.21 or 1 : 1 or, in percentages, 50 : 50. This proportion is very close to the accepted value (p. 32), 32.06 : 32.

The same method could be used for carbon, for the carbon dioxide produced would be absorbed in the solution of potassium hydroxide.

Combustion. — Violent union with oxygen is called, in popular language, **combustion** or burning. Yet, since oxygen is only one of many gaseous substances known to the chemist, and similar vigorous interactions with these gases are common, the term has no scientific significance. Even the union of iron and sulphur gives out light and heat, and is quite similar in the chemical point of view to combustion.

A misleading term often used in this connection is **kindling temperature.** It gives the impression that there is a definite temperature at which combustion will start. But the temperature is only *one* of the conditions which produce combustion. Finely powdered iron will start burning at a lower temperature than will an iron wire, *because it presents relatively more surface to the gas.* Again, if the oxygen is at less than one atmosphere pressure, the wire will require to reach a higher temperature before combustion will begin. Finally, the vapor of methyl alcohol and air requires to be raised above a red heat before combustion starts, but a pocket cigar-lighter sets fire to this very mixture by means of a contact agent (a thin platinum wire) without any other means of heating being required. So that, the conditions under which combustion begins involve the physical condition of the solid, the pressure of the gas or vapor, the presence or absence of a contact agent and the nature of the contact agent, as well as the temperature. No definite kindling temperature can be given, unless the other conditions are specified also. Kindling conditions involve several variables, of which the temperature is only one.

Oxidation. — The slower union with oxygen which occurs in rusting is called **oxidation.** We shall see later, however, that it has been found convenient to stretch this term so as to cover combinations of other elements than oxygen, and even to include actions not involving combination. At this point we can discuss only oxidation by oxygen.

This process of slow oxidation by oxygen, although less conspicuous than combustion, is really of greater interest. Thus the **decay of wood** is simply a process of oxidation whereby the same products are formed as by the more rapid ordinary combustion. **Sewage** is mixed with large volumes of river water, the object being, not simply to dilute the sewage, but to mix it with water containing oxygen in solution. This has an oxidizing power like that of oxygen gas and, through the agency of bacteria, quickly renders dissolved organic matters innocuous by converting them for the most part into carbon dioxide and water. Thus, a few miles further down the stream, the water becomes as suitable for drinking as it was before the sewage entered. **In our own bodies** we have likewise a familiar illustration of slow oxidation. Avoiding details, it is sufficient to say that the oxygen, from the air taken into the lungs, combines with the hæmoglobin in the red blood-corpuscles. In this form of loose combination, it is carried by the blood throughout our tissues and there oxidizes the foodstuffs which have been absorbed during digestion. The material products are carbon dioxide and water, of which the former is carried back to the lungs by the blood, and finally reaches the air during exhalation. The important product, however, is the heat, given out by the oxidation, which keeps the body warm.

The opposite of oxidation, the *removal* of oxygen, is spoken of in chemistry as **reduction.** But this term, also, has been stretched to cover other kinds of chemical change.

Spontaneous Combustion.—Sometimes a mere slow oxidation develops into a combustion, which is then known as **spontaneous combustion.** To understand this, we must note the fact that a given weight of material, say, iron, in combining with oxygen to form a given oxide, will liberate the same total amount of heat whether the union proceeds rapidly or slowly. If the action proceeds slowly, and the material being oxidized is freely exposed to the air, the latter will become heated and will carry off the heat as fast as it is produced. Thus, no particular rise in temperature will occur. If, however, the material is a poor conductor of heat, like hay or rags, and there is sufficient air for oxidation, but not enough to carry off the heated air, the heat may accumulate and a temperature sufficient to start combustion may be reached. Such a situation sometimes arises in hay-stacks. It occurs also when rags, saturated with oils used in making paints (linseed oil and turpentine) are left in a heap. These oils, in "drying," combine with oxygen from the air and turn into a tough, resinous material. The rags, being poor conductors of heat, finally become hot enough to burst into flame, and serious conflagrations often owe their origin to causes such as this. Oily rags should always be disposed of by burning, or should at least be placed in a closed can of metal. Fires in coal bunkers of ships arise from the same cause — slow oxidation, with accumulation of the resulting heat. That coal does undergo slow oxidation, especially when freshly mined, is shown by the fact that such coal, if left exposed to the air for months, may lose 10 per cent or more of its heating power.

Uses of Oxygen.—A number of the practical applications of oxygen have already been mentioned. For example, in the foregoing section we have referred to its use in breathing, its rôle in decay, which is a beneficent process because it removes much useless matter which might otherwise cause disease, and its value in the disposal of sewage. Power and heat for commercial purposes are almost all obtained by the burning of coal, in which oxygen from the air plays a large part. If we had to purchase the oxygen as well as the coal, we should require at least three tons of oxygen for every ton of coal.

Oxygen in cylinders and oxygen generators are used to restore the supply in the atmosphere of submarine boats, as well as for the purposes already mentioned (p. 27).

Substances Indifferent to Oxygen. — Finally, since the atmosphere contains so large a proportion of oxygen, substances which do *not* oxidize and, when heated, do *not* burn, have many uses. Gold, silver, and platinum are of this kind (p. 32), and are used for ornaments. The last is used for crucibles in which bodies are heated in the laboratory. Although iron burns in pure oxygen, it does not oxidize rapidly in the air even when heated, and so is used for making vessels for cooking and in constructing fireproof buildings.

Compounds, already fully oxidized, are naturally not combustible. Of this nature are sandstone, granite, brick, porcelain, glass, and water. All these are, therefore, fireproof. Moreover, these substances do not give off oxygen when heated (water decomposes slightly). Glass and porcelain thus neither lose nor gain in weight when heated, and are suitable materials for laboratory apparatus.

Activity and Stability. — A substance which enters into combination vigorously, as does oxygen, is called chemically **active.** Nitrogen, on the other hand, is relatively **inactive.** An active element, since it combines eagerly, naturally holds tenaciously to the matter with which it has combined. An active element implies, therefore, also one which is in general difficult to liberate from combination. Its compounds are in general relatively **stable.** Thus, many oxides, and the natural compounds just mentioned (sandstone, granite, brick and porcelain, the last two made from clay), do not lose oxygen even at a white heat and are very *stable.*

Exercises. — 1. What percentage by weight of free oxygen is obtained by heating: (*a*) mercuric oxide, (*b*) potassium nitrate, (*c*) potassium chlorate? At $1.50 (7/8), $0.15 (8d), and $0.15 (8d) per kilogram, respectively, which is the cheapest source of oxygen?

2. Using the data on pp. 30–31, calculate the weight of oxygen dissolved by 1000 c.c. of water at 0°.

3. Why does a forced draft make a fire burn more rapidly?

4. Why does a naked flame sometimes cause an explosion in a mine, when the air of the mine is filled with coal dust?

5. The substances, like phosphorus and sulphur, which burn rapidly in ordinary oxygen, combine very, very slowly with oxygen which has been freed from moisture by careful drying. How is this effect of water to be classified?

6. Air is 20 per cent oxygen. Why does iron burn brilliantly in pure oxygen, but not in air?

CHAPTER IV

ATOMIC WEIGHTS, SYMBOLS, FORMULÆ, AND EQUATIONS

WE have repeatedly called attention to the *quantities* of the substances taking part in chemical changes, and particularly to the constant relation between the weights of each element in a given substance (pp. 17–18). This matter is of great importance in chemistry. If a cargo of copper ore is to be purchased, we do not wish to pay for the rock that all specimens of the ore contain in larger or smaller proportion. So we secure a fair sample of the ore and have an **analysis** made by a chemist. The analysis, in this case, is a measurement of the proportion of the valuable metal in the sample. The price will then depend largely upon the proportion of the copper per ton of ore. The making of analyses — that is, chemical measurements — plays a very large part in all industries which involve the consumption or manufacture of materials. Quantitative measurements, aside from their theoretical interest, are therefore of the greatest practical importance. Hence we must now discuss them once more.

The Compositions of Substances. — Our present purpose is to compare the proportions by weight of the elements composing several compounds, in order to see whether the numbers are really as irregular as, in the examples we have heretofore given, they have appeared to be, or whether there is any way of relating and simplifying the numbers.

In order to have a fair sample of these proportions, we shall include the compositions of a few substances for which the data have not yet been given. Potassium hydroxide (p. 35) has the composition: potassium (a metal) 39.1, oxygen 16, hydrogen 1.008, in a total of 56.108 parts. Water (oxide of hydrogen) contains: oxygen 16 and hydrogen 2.016 parts by weight. When iron burns in chlorine, which is a yellow gas, it gives ferric chloride with the proportions: iron 55.84, chlorine 106.38. When ferric chloride is heated in a stream of hydrogen gas, a part of the chlorine is removed, and ferrous chloride remains: iron 55.84, chlorine 70.92.

To make the comparison easy, we have limited the number of substances to five of those previously discussed, together with the four just mentioned, and have also arranged the proportions in the form of a table.

PROPORTIONS BY WEIGHT OF THE ELEMENTS IN CERTAIN COMPOUNDS

Name of Compound.	Iron.	Oxygen.	Sulphur.	Potassium.	Chlorine.	Hydrogen.
Ferric oxide (p. 9)	111.68	48	....	....	....	....
Ferrous sulphide (p. 14)	55.84	....	32.06	....	....	....
Potassium chlorate (p. 27)	....	48	....	39.1	35.46	....
Sulphur dioxide (p. 32)	....	32	32.06	....	....	....
Iron oxide (magnetic) (p. 32)	167.52	64	....	....	....	....
Potassium hydroxide	....	16	....	39.1	....	1.008
Water	....	16	....	....	....	2.016
Ferric chloride	55.84	....	....	....	106.38	....
Ferrous chloride	55.84	....	....	....	70.92	....
Atomic weights	55.84	16	32.06	39.1	35.46	1.008

Study of the Foregoing Table. — When we first examine the numbers in the horizontal lines of the table, we observe that the numbers, with the exception of those for oxygen, all involve decimal fractions. From this we infer that whole numbers must have been chosen intentionally for oxygen. This is, in fact, the case. When we next look *down* the oxygen column, we observe that 48 = 3 × 16 and 32 = 2 × 16 and 64 = 4 × 16. All the oxygen weights are multiples of 16 by some integral (whole) number. In the hydrogen column, the same regularity appears, for 2.016 = 2 × 1.008. Following up this idea, we find in the iron column, 55.84 occurring thrice, and discover that 111.68 = 2 × 55.84, and that 167.52 = 3 × 55.84. Similarly, in the chlorine column, the numbers are multiples of 35.46 by unity or some other integer. Thus, the proportion of each element, in various compounds, can be represented by a fundamental number — a sort of *unit quantity* — multiplied when necessary by the proper integer.

Now this rule is not confined to these nine compounds, involving only six different elements. If we provided a column for every known element (about eighty would be needed), and entered the composition of every known compound, we should find the same rule to hold. This rule can be stated as follows:

Law of Combining Weights. — **In every compound substance, the proportion by weight of each element may be expressed by a fixed number, a different one for each element, or by a multiple of this number by some integer** (whole number).

Since the proportion by weight in which two (or more) elements combine is a chemical property, this is a chemical law. Clearly, it does not apply to mixtures, for any irregular proportion could be used in the physical process of mixing.

Explanation of this Law, Atoms and Atomic Weights. — To explain this law it was necessary to use the third kind of explanation (p. 23), namely the making of an hypothesis. The details of *how* two substances combine cannot be seen, so chemists had to *imagine* some details which would account for the possession of an individual unit weight by each element. If oxygen *is composed of minute, invisible particles*, which are *all alike in weight*, and hydrogen and potassium are of the same nature, except that *the weight of the particle of each kind of element is different*, we have the basis of an explanation. We have to suppose, further, that, when elements combine, *the particles adhere in pairs or groups, as wholes, and are never broken.* In this way the *particle* of each variety of elementary matter will have a definite, unchangeable weight, which will be one of its fixed properties. If the relative weights of the *particles* of oxygen, potassium, and hydrogen are in the proportion of the combining numbers in the table, namely 16 : 39.1 : 1.008, the whole situation becomes clear. Chemical union must consist, in detail, in the union of the particles of the elements to form the particles of the compound. For each particle of potassium hydroxide, *one particle each* of the three elements is required.

For each particle of water, where the proportion of oxygen to hydrogen is 16 : 2.016, evidently one particle of oxygen and *two* particles of hydrogen are necessary. Varying, intermediate proportions are impossible, because the particles of the elements are permanent, are never broken, and combine as wholes, and in a uniform way through the mass. The only possible variation would be to take different relative numbers of the particles — for example, two of oxygen to two of hydrogen (2 × 16 : 2 × 1.008). But this product would have a different composition from water, and would not be water. This compound, with the double proportion of oxygen, is indeed known (it is hydrogen peroxide), and is the only other known compound of these two elements.

This theory fully explains why the combining proportions of each element, in different compounds, can always be expressed by a fixed, unit number (which represents the weight of the ultimate particle of that element), multiplied, when necessary, by a whole number (representing the number of particles of the element required to form a particle of the compound in question).

This explanation was first offered by Dalton, a schoolmaster of Manchester in 1802. Borrowing an idea from the speculations of the Greek philosophers, he called the particles of *elements* **atoms** (Gk., *not cut*, or *not divided*). The atoms of any one element are all alike in weight, as well as in other properties, but the atoms of different elements differ in weight.

The particles made by uniting two or more atoms, as in forming a particle of a *compound*, are called **molecules** (Gk., *a little mass*).

A chemical combination of two simple substances consists, then, in an elaborate re-grouping of the atoms of both elements so that molecules of the compound are formed. Definite proportions by weight are required, in order that the atoms of each element may be available in the correct proportion, 1 atom : 1 atom, or 1 : 2, or 2 : 3, or in some similar, usually simple ratio.

The result was called the **atomic theory.** For long it remained an hypothesis, or sort of guess. Recently, however, we have obtained independent proof that molecules and atoms are real (see Radioactivity), for we can now count and measure the weight of individual molecules, and we even know something of the *inside* structure of atoms.

The fundamental numbers, one for each element, being **the relative weights of the atoms,** are called **atomic weights.**

Symbols and Formulæ. — One self-evident use for the atomic weights is in stating the compositions of compounds. To make the statement as simple as possible, **symbols**, first used by Berzelius, **represent the atomic weight of each element.** Thus, H stands for 1.008 parts, or 1 atom, of hydrogen, and O for 16 parts, or 1 atom, of oxygen. When several elements have the same initial letters, another letter is added: C for one atomic weight of carbon, Ca for one atomic weight of calcium, Cl for 35.46 parts of chlorine. When the names of the elements are not alike in all languages, the symbol is frequently based on the Latin name, as Fe for iron (*ferrum*) and Pb for lead (*plumbum*), or on the German, as K for potassium (*kalium*). The symbols are international. A list of the elements, with their symbols and atomic weights, is printed inside the back cover of this book.

The composition of any compound can thus be stated by setting down the necessary symbols, together with the whole numbers, if any, by which the atomic weights are multiplied. The result is a **formula.** For example, ferric oxide contains iron 111.68 and oxygen 48 parts (p. 41). This is equivalent to iron 2 × 55.84 and oxygen 3 × 16. This again is equivalent, in symbols, to 2 × Fe and 3O. The formula is written Fe_2O_3. Ferrous sulphide is a simpler case: iron 55.84 and sulphur 32.06, or, in symbols, FeS. The reader should now examine the whole table on p. 41, and work out the formula of each compound and write it in the margin.

Equations. — It is now possible to abbreviate the condensed statements we have been using to represent the substances and their quantities in chemical reactions. Thus, the three statements on p. 32, when translated into symbols, are as follows:

$$S + 2O \rightarrow SO_2.$$
$$2P + 5O \rightarrow P_2O_5 \quad (P = 31.04).$$
$$C + 2O \rightarrow CO_2 \quad (C = 12).$$

When no coefficient appears before or after a symbol, 1 is to be understood.

Much practice is required to enable one to make and understand equations. The reader should therefore at once turn back to the statements on pp. 9, 14, 17, 27, and 28, obtain the necessary atomic weights and symbols from the table at the end of the book, and construct the equation in each case.

The term "equation" refers to the fact that the total weight of matter on both sides is always the same. In other respects, such as in the nature of the substances, the two sides are entirely different.

Derivation of Formulæ from Experimental Data.—In the condensed statements referred to (by page) in the foregoing section, the numbers given were already multiples of the atomic weights, and the formulæ were therefore easy to make. It remains to show how the formula may be constructed from the weights obtained in an experiment.

In the quantitative experiment on the composition of cupric oxide (p. 34), the proportion found was: copper 85, oxygen 21. In the formula, the same proportion is to be expressed by means of multiples of the atomic weights. If we divide each of these numbers by the corresponding atomic weight, the quotient will be the number by which the atomic weight must be multiplied. The atomic weights are Cu = 63.57, O = 16. 85 ÷ 63.57 = 1.3, and 21 ÷ 16 = 1.3. The proportion of copper to oxygen in the compound, $\frac{85}{21}$, now becomes $\frac{63.57 \times 1.3}{16 \times 1.3}$.

But this proportion must be expressed in multiples of the atomic weights by *whole* numbers. Dividing above and below by 1.3, we get $\frac{63.57 \times 1}{16 \times 1}$.

Now the symbols stand for the atomic weights. Substituting the symbols, the proportion becomes $\frac{\mathrm{Cu} \times 1}{\mathrm{O} \times 1}$. The formula is, therefore, CuO.

Applying the same process to the case of sulphur dioxide (p. 35):

$$\frac{\text{Sulphur}}{\text{Oxygen}} = \frac{32.06}{32} = \frac{32.06 \times 1}{16 \times 2} = \frac{\mathrm{S} \times 1}{\mathrm{O} \times 2}, \text{ or } SO_2.$$

If the composition of the substance has been stated in percentages, the same device is used. Thus, the case of sodium sulphate works out as follows:

Elements.	Percentages.	At. Wt. Quotient	÷	Formula.
Sodium	32.43	23 × 1.41	0.705	Na × 2
Sulphur	22.55	32 × 0.705	0.705	S
Oxygen	45.02	16 × 2.814	0.705	O × 4

The formula is, therefore, Na_2SO_4.

It is obvious that, after we have found out what elements compose a given compound, we are still unable to write its formula. We may *not* simply set the symbols down, side by side. A measurement must be made, in order that we may find out the factors by which the atomic weights are to be multiplied.

Answers to Some Questions. — Why was a *whole* number assigned to oxygen? Oxygen was chosen as the basis of the system because the exact determinations of the combining weights of most of the elements have actually been made by direct union with oxygen, or with the help of but one intermediate step. If the question had been one of mathematics, hydrogen, the element with the lowest combining proportions, would have furnished the basis and unit of the scale. But the question was the practical one of getting the most accurate measurements for the relative magnitudes of the numbers. Hydrogen combines with only a few of the elements, and the proportion of hydrogen is usually so small that the weights of this element cannot be measured so accurately as can the much larger weights of oxygen and of the other elements. So oxygen was selected as the basal element.

Why was 16 assigned to oxygen, rather than 1 or 100, or some other whole number? The number 16 was chosen in order that the advantage of having a mathematical unit, or something close to it, in the scale, might be retained also. With this value, hydrogen became 1.008. A whole number smaller than 16 would make the atomic weight of hydrogen less than unity. With $H = 1$, the value for oxygen becomes about 15.9, and the values for all the elements are changed in proportion. The result of such a change would be that the values for the common elements would not be so close to whole numbers as they at present are (*e.g.*, $C = 12.00$, $N = 14.01$, Na (sodium) $= 23.00$, $K = 39.1$, $P = 31.04$). With

$O = 16$, it is possible, and of course more convenient, in many cases to use the nearest whole number in ordinary calculations.

The answers to the two foregoing questions show why the scale of the numbers was fixed as it is. Of course, multiplying or dividing all the atomic weights by any number, whole or fractional, would not affect their scientific accuracy. The choice of scale is merely a matter of convenience.

In physics there is one unit of weight, the gram, for all kinds of matter. Is it the case that in chemistry a different unit of weight is employed for each element? This is the exact situation, and it is one peculiar to chemistry. It does not represent an arbitrary decision of the chemist, however. It is due to the fact that the atoms of any one element have the same weight, but that the atoms of different elements have different weights. The atom of uranium is 238 times as heavy as that of hydrogen, and its combining proportions, therefore, are in general greater in the same ratio, while the atoms of the other elements have weights falling between these limits.

There is still one question to be asked. Why take 16 for oxygen rather than 8 or 32? In other words, may we not multiply or divide any *one* (or more) of the *individual* atomic weights by a whole number? The answer is that, *thus far*, we have not met with any reason for not doing so. With $O = 8$, and H still 1.008, the composition of water would be represented by the formula HO instead of H_2O (where $O = 16$). In a *later* chapter (Chap. VIII), however, we shall see that the individual numbers actually chosen meet certain other conditions, in addition to those already mentioned, and are on that account preferable to any other set.

Law of Multiple Proportions. — We have already met with several instances in which two elements combine in more than one proportion by weight, and form therefore more than one compound. Thus two oxides of iron and two chlorides of iron have been mentioned (p. 41), and two oxides of hydrogen, water and hydrogen peroxide, are known (p. 43). This general fact was discovered before the law of combining weights (p. 42) had been formulated, and is a particular case of this law. It was discovered by Dalton (1804) and was embodied by him in a statement known as the **law of multiple proportions**, which ran somewhat as follows:

If two elements unite in more than one proportion, forming two or more compounds, the quantities of one of the elements, which in the different compounds are united with identical amounts of the other, stand to one another in the ratio of integral numbers, which are usually small.

The two chlorides of iron illustrate the law. Ferric chloride contains iron 55.84 and chlorine 106.38, and ferrous chloride iron 55.84 and chlorine 70.92. Thus the quantities of chlorine united with identical amounts of iron (namely, 55.84 parts) stand in the ratio 106.38 : 70.92, or 3 : 2.

Exercises.—1. From the data on p. 9 and the atomic weights, calculate the formula of lead oxide. Construct also the equations for the decomposition of potassium chlorate (p. 27), and for the combination of phosphorus and oxygen (p. 32).

2. When 1 g. of sodium burns in oxygen, it produces 1.7 g. of the oxide. What is the formula of the latter and the equation?

3. If 26 g. of mercurous oxide are required to give, by heating, 1 g. of oxygen, what is the formula of the substance?

4. What are the formulæ of the substances possessing the following percentage compositions?

I		II		III	
Magnesium,	25.57	Sodium,	32.43	Potassium,	26.585
Chlorine,	74.43	Sulphur,	22.55	Chromium,	35.390
		Oxygen,	45.02	Oxygen,	38.025

5. What are the percentage compositions of substances possessing the following formulæ: Mn_3O_4, KBr, $FeSO_4$?

6. Compare the formula of mercurous oxide, found in 3, with that of mercuric oxide, and show how the compounds illustrate the law of multiple proportions (p. 48).

7. If the atomic weight of potassium were 13.03, and the other atomic weights were unchanged, what would be the formulæ of (*a*) potassium hydroxide, and (*b*) potassium chlorate?

CHAPTER V

HYDROGEN

Having learned something of the nature of the atmosphere, and particularly of oxygen, its most active component, we turn now to water, a substance as closely connected with our daily life as is air. We find that it is a compound of oxygen and hydrogen, and the latter element, therefore, may be taken up next. Hydrogen is of interest on its own account because it is often used in filling balloons, and nearly half the bulk of ordinary illuminating gas is free hydrogen.

History. — That hydrogen is a distinct kind of gas was first established by Cavendish (1766). Somewhat later (1781), he showed that, when it burned in the air, it gave a vapor which could be condensed to liquid water. Since oxygen was then known to be the substance with which combustibles united, this proved that water was a compound of hydrogen (Gk., *water producer*) and oxygen.

Occurrence. — Free hydrogen is found, mixed with varying proportions of other gases, in exhalations from volcanoes, in pockets found in certain layers of the rock-salt deposits, and in some meteorites. The air contains not over 1 part in 1,500,000. The lines of hydrogen are prominent in the spectra of the sun and of most stars.

In combination, it constitutes about 11 per cent of water. It is an essential constituent of *all* acids. It is contained also, in combination with carbon, in the components of natural gas, petroleum, and all animal and vegetable bodies.

Preparation by the Action of Metals on Cold Water. — To liberate hydrogen from water, it is necessary to use some element with which the oxygen of the water will combine even more eagerly than with hydrogen, and to offer this element in exchange for the hydrogen.

The more active metals, such as potassium (K), sodium (Na), or calcium (Ca), displace hydrogen rapidly from **cold water.** Potassium and sodium are lighter than water, and float on the surface. In the case of the former, so much heat is liberated that the hydrogen catches fire, and with neither metal is the experiment safe in the hands of a novice. Calcium sinks to the bottom, and acts rapidly, but not violently, so that the gas is easily collected (Fig. 22). The pieces of these metals, of course, act upon only a small part of the water in the vessel. In each case the metal displaces one-half only of the hydrogen in that part of the water upon which it acts. The other products are the hydroxides of potassium, sodium, and calcium, respectively. The two former dissolve, leaving a clear liquid when the metal is all gone, but may be recovered as white solids by evaporation. The calcium hydroxide (slaked lime) is dissolved only in part, and much of it may be seen suspended in the water after the action.

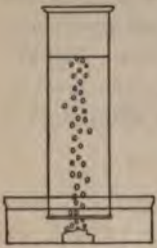

FIG. 22.

An alloy of lead with sodium (35 per cent), sold under the name of **hydrone,** affords a convenient substitute for sodium in the foregoing actions.

The Making of Equations. — To make an equation we must have the results of quantitative measurements. These furnish us with the composition of each substance concerned. The composition, expressed in multiples of the atomic weights, is recorded in the formula for the substance. If we are in possession of the necessary formulæ, we can write the equation.

For example, the composition of water is: hydrogen 2 × 1.008, oxygen 16. In symbols, this is 2H and O, and the formula is, therefore, H_2O. The composition of potassium hydroxide is: potassium 39.1, oxygen 16, hydrogen 1.008, and the formula, therefore, KOH. In calcium hydroxide the proportions are: calcium 40.07, oxygen 2 × 16, hydrogen 2 × 1.008, and the formula $Ca(OH)_2$.

To make the equation, we first write down the formulæ of the substances used and produced:

$$K + H_2O \rightarrow KOH + H.$$

$$Na + H_2O \rightarrow NaOH + H.$$

Skeleton: $$Ca + H_2O \rightarrow Ca(OH)_2 + H.$$

Next we must **balance this equation,** if necessary. That is, we must adjust it so that there are equal numbers of atomic weights (or atoms) of each element on both sides of the equation. This is necessary only in the third equation, and is done because, according to the law of conservation of mass, there must be the same quantity of each element after the reaction as there was before it. On examining the third equation, we note that there is 2O, in the $(OH)_2$, on the right side and only O on the left. We therefore place a 2 in front of the H_2O, for we cannot get the additional oxygen excepting by using more water:

Balanced: $Ca + 2H_2O \rightarrow Ca(OH)_2 + 2H.$

The number of atomic weights of hydrogen is made equal by using 2H on the right side.

The coefficients *in front* of a formula multiply the *whole* formula. Thus, $2H_2O$ is equivalent to $2(H_2O)$. A subscript coefficient *following* a symbol, however, multiplies that symbol only. Thus H_2O is equivalent to $(H)_2O$, or $(2 \times H + O)$.

Four Steps in Making an Equation.—1. Find out, by observation and experiment, *what substances are used* and what substances are *produced.*

2. Find the *formula* of *each substance* used or produced.

3. Set the formulæ down as a skeleton equation, placing the formulæ of the *substances used* on the *left,* and of those *produced* on the *right.*

4. Adjust, or *balance* the equation, if necessary.

The reader must *practice* the making of equations, until he can do it quickly. The text contains many equations, but more usually only the data required for making them (the formulæ of the substances) are given.

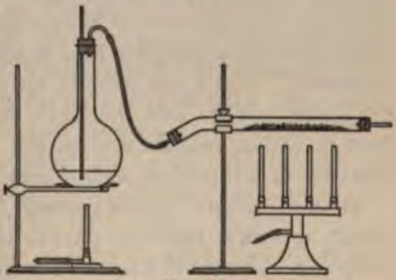

FIG. 23.

Hydrogen from Metals and Water at a High Temperature.—With **steam** at a red heat, metals like iron, zinc, and magnesium interact vigorously. The steam, generated in a flask, enters at one end of the tube containing the metal (Fig. 23), and the hydrogen passes off at the other. Since, at a red heat, all hydroxides, except those of potassium and sodium, are decomposed into an oxide of the metal and water, as, for example, $Mg(OH)_2 \rightarrow MgO + H_2O$, the *oxides* are formed in this case:

$$Mg + H_2O \rightarrow MgO + 2H.$$

Iron gives the magnetic oxide Fe_3O_4.

Making Equations, Again. — The skeleton equation for the action of iron on steam is:

Skeleton: $$Fe + H_2O \rightarrow Fe_3O_4 + H.$$

We are not permitted to alter these formulæ themselves, but we may put coefficients in front of any of them to make the number of atomic weights alike on both sides. A useful rule is *to pick out the largest formula* and reason back from that. Here, this is Fe_3O_4. To get Fe_3, we must start with 3Fe, and to get O_4, we must start with $4H_2O$:

Balanced: $$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H.$$

Acids. — In making hydrogen in the laboratory, the acids are used almost exclusively. The common acids are **hydrochloric acid** (HCl, Aq), and **sulphuric acid** (H_2SO_4, Aq). The usual forms are mixtures containing water, the *variable* amount of the latter being indicated by the symbol Aq.* The former is a solution of a gas, hydrogen chloride. The "pure concentrated" hydrochloric acid used in laboratories contains nearly as much of the gas (39 per cent by weight) as the water can dissolve. The "commercial" acid contains impurities and is also less concentrated. The "concentrated" sulphuric acid is an oily liquid containing practically no water. The "commercial" sulphuric acid contains 6 to 7 per cent of water, besides impurities. **Acetic acid** (HCO_2CH_3, Aq) is a solution of a liquid in water, and is the acid found in vinegar.

All the "dilute" acids contain 70 to 80 per cent of water. The water, as a rule, takes no part in the chemical changes in which the acids are concerned, and is therefore omitted from the equations.

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* The formula H_2O stands for a fixed proportion of water, namely 18 parts. The water in these solutions is not combined, and can be varied in amount, so that the formula H_2O may not logically be employed here.

The name "acid" is restricted to one class of substances having certain definite characteristics. Hydrogen is the one essential constituent of all acids. Their aqueous solutions have a sour taste and change the color of litmus from blue to red. When free from water they do not conduct electricity. When dissolved in water they conduct, and are decomposed by the electric current. In aqueous solution, also, their hydrogen (or one unit weight of it in the case of acetic acid) is displaced by certain metals.

Radicals.—In describing the chemical behavior of acids, we speak of the hydrogen as the **positive radical,** because in electrolysis (see p. 55) it is attracted to the negative pole, and of the material combined with the hydrogen as the **negative radical,** because it is attracted to the positive pole. Thus the negative radicals in the above acids are Cl, SO_4, and CO_2CH_3, respectively. The first (Cl) is a simple radical, the others are compound radicals. In many interactions the compound radicals move as units from one state of combination to another.

Preparation by Displacement from Diluted Acids.—Every one of the metals which displace hydrogen from water will also displace it from dilute acids. The acids *must be diluted with water,* unless, like hydrochloric acid, they are already dissolved in water. The action is much more vigorous than that on water, so that the most active metals are not employed. Metals like zinc, iron, and aluminium serve the purpose. The metal combines with the negative radical, and so liberates the hydrogen, which escapes in bubbles. Evaporation of the clear liquid, when the metal has all disappeared, gives in dry form the compound of the metal with the negative radical. Thus, with zinc and dilute sulphuric acid, zinc sulphate $ZnSO_4$ is produced.

Skeleton: $Zn + H_2SO_4 \rightarrow ZnSO_4 + H.$

Balanced: $Zn + H_2SO_4 \rightarrow ZnSO_4 + 2H.$

With aluminium and hydrochloric acid, the product is aluminium chloride $AlCl_3$:

Skeleton: $Al + HCl \rightarrow AlCl_3 + H.$

Balanced: $Al + 3HCl \rightarrow AlCl_3 + 3H.$

The water undergoes no change during the action, although its presence is essential. It is simply a part of the apparatus. Any acid may be used, although with many the action goes on very slowly.

For preparing small amounts of hydrogen, the apparatus (Fig. 24) is such that additional acid may be added through the thistle-, or safety tube. This avoids opening the flask and admitting air. The gas may be caught like oxygen over water or, being lighter than air, may be collected by **downward displacement** of the latter (Fig. 25a). Heavy gases are collected by **upward displacement** of air (Fig. 25b).

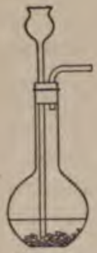


FIG. 24.

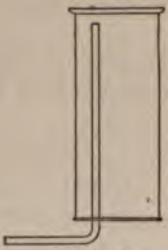


FIG. 25a.

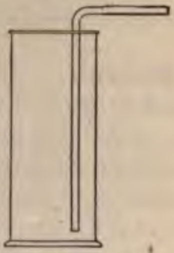


FIG. 25b.

With a Kipp's apparatus (Fig. 26) the gas may be made on a large scale and its delivery can be regulated. When the stream of gas is shut off by the stopcock, the pressure of the gas, as it continues to be generated, drives the acid away from the metal and up into the globe above, so that the action ceases. Yet the action is ready to begin again the moment any portion of the stored gas is drawn off for use.

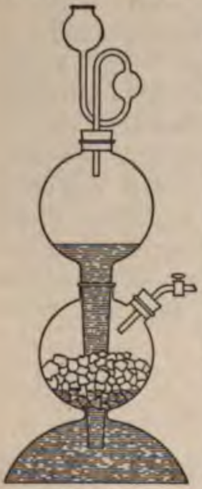


FIG. 26.

Silver, gold, and platinum, which do not combine with free oxygen, and even copper and mercury, which do, are all *unable* to liberate hydrogen and to form oxides when heated in steam. When treated with dilute acids, none of these metals is able to displace and liberate the hydrogen (see order of activity of the metals, p. 59).

Contact of the zinc or iron with an inactive metal, like platinum or copper, forms an electrical couple and hastens the interaction. For the same reason, commercial zinc, which contains traces of other metals, gives a steady evolution of hydrogen, while extremely pure zinc is almost inactive.

The Third Variety of Chemical Change: Displacement. — The reactions used in liberating hydrogen illustrate the third of the four common forms of chemical change. Here **a simple substance** (the metal) **and a compound** (the acid) **interact; the compound is divided into its radicals; and the simple substance combines with one radical while the other radical is liberated.** The interacting element, here the metal, is said to **displace** the other element, here the hydrogen, from combination. The action of metals on water is a displacement also.

Preparation of Hydrogen by Electrolysis. — If we dissolve *any acid* in water, and immerse the wires from a battery in the solution, bubbles of hydrogen begin to appear on the *negative* wire (the cathode) and rise to the surface. All the other constituents, whatever they may be, are attracted to the positive wire (the anode) and, therefore, do not interfere with the collection of pure hydrogen. An apparatus devised by Hofmann (Fig. 27) enables us to secure the hydrogen, which ascends on the left and accumulates at the top of the tube, displacing the solution. When hydrochloric acid is used: $HCl \rightarrow H$ (neg. wire) $+ Cl$ (pos. wire), the chlorine, a soluble gas, remains dissolved in the water near the positive pole. When sulphuric acid is employed:

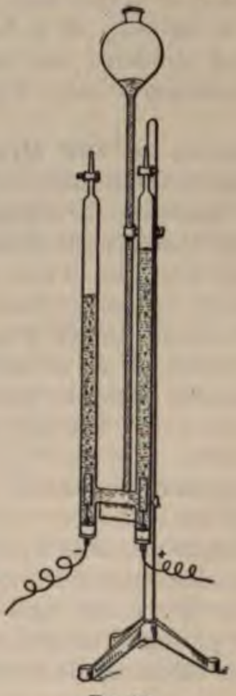


FIG. 27.

$$H_2SO_4 \rightarrow 2H \text{ (neg. wire)} + SO_4 \text{ (pos. wire)}. \qquad (1)$$

The SO_4, however, acts upon the water:

$$SO_4 + H_2O \rightarrow H_2SO_4 + O. \qquad (2)$$

Thus, the sulphuric acid is re-formed, round the positive wire, and only hydrogen and oxygen are finally liberated.

Decomposition of a compound by the use of electrical energy is called **electrolysis** (Gk., *decomposition by electricity*).

The Other Ways of Preparing Hydrogen. — For special purposes, hydrogen may be made by boiling an aqueous solution of sodium hydroxide with aluminium turnings, when sodium aluminate is formed: $Al + NaOH + H_2O \rightarrow NaAlO_2 + 3H$; also by heating powdered zinc and dry sodium hydroxide, the product being sodium zincate: $Zn + 2NaOH \rightarrow Na_2ZnO_2 + 2H$.

Sources of the Hydrogen of Commerce. — Zinc is too expensive a substance to use in the preparation of hydrogen in large quantities for commercial purposes. We realize this when we note that 33 parts of zinc will liberate only one part of hydrogen, so that with 1 lb. of zinc we obtain only one half-ounce of the gas. Different sources are used in different localities and countries.

The largest supply is probably obtained as a by-product in the electrolysis of an aqueous solution of common salt ($NaCl$), in connection with the manufacture of caustic soda (sodium hydroxide, *q.v.*). The hydrogen is collected and compressed in steel cylinders.

In some circumstances, the method of passing steam over heated iron is used (p. 51).

Another plan is to liquefy water-gas (*q.v.*), a mixture of hydrogen and carbon monoxide. The hydrogen evaporates much the more readily of the two, and can thus be separated. This, and still other processes, involve substances and reactions which we have not yet encountered and will be mentioned at the appropriate points.

Physical Properties. — Hydrogen is a colorless, tasteless, odorless gas. One liter weighs only 0.08987 g., while one liter of air weighs 1.293 g. Air is thus 14.5 times heavier, and hydrogen can be poured upwards (Fig. 28) and is used for filling balloons. Hydrogen was first liquefied in visible amounts by Dewar (1898).

The critical temperature is −234°. The colorless liquid boils at −252.5° and, when allowed to evaporate rapidly under reduced pressure, freezes to a colorless solid (m.-p. −260°). All other gases, except helium, solidify easily when led into a vessel surrounded by liquid hydrogen.

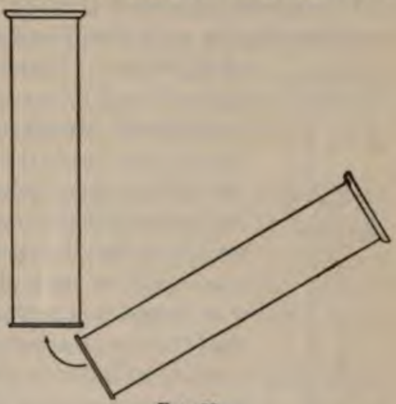


FIG. 28.

Hydrogen is even less soluble in water than is oxygen, 1.8 volumes of the gas dissolve in 100 volumes of water at 15°. Hydrogen is absorbed, for the most part in a purely mechanical way, by many metals. Heated iron will take up 19 times its volume of hydrogen, gold takes up 46 volumes, platinum in fine powder 50 volumes, palladium 502 volumes, and silver none. The maximum absorbed by palladium under favorable conditions is 873 volumes.

Diffusion. — When two cylinders, one filled with hydrogen and one with air, are placed mouth to mouth (Fig. 29), so that the one containing hydrogen is uppermost, since the air in the lower cylinder is 14.5 times heavier than the hydrogen, we might expect the gases to remain in their respective cylinders. The air, however, makes its way into the hydrogen above it, and the hydrogen penetrates into the air in the lower cylinder so that, in a short time, the gases are perfectly mixed, just as if gravity did not exist. The same phenomenon is observed when, in everyday life, a bottle of scent is opened. The vapor, on escaping, begins to penetrate in all directions through the room, showing its presence by its odor. The material of gases has in fact an independent power of locomotion. The resulting phenomenon we call *diffusion.* It is constant in rate for each gas under like conditions, and hydrogen has the greatest speed of diffusion of all the gases.

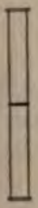


FIG. 29.

The different rates of diffusion of different gases are easily shown by comparing their several speeds with that of air, when both pass through a wall of unglazed, porous porcelain.

The porous cylinder *A* (Fig. 30) contains air and is connected by a rubber stopper with a wide tube which dips beneath the surface of the water. When a cylinder *H* containing hydrogen is brought over it, rapid escape of gas takes place through the water, showing that a rise in pressure has taken place inside the porous vessel. Before the cylinder of hydrogen approached the porous vessel, the air was moving both outwards and inwards through the porcelain, but, being the same air, the speed of motion was equal in both directions, and therefore the pressure inside was not affected. It is important to note that there was at no time rest, there was simply equal motion in both directions. When the hydrogen atmosphere surrounded the cylinder, the hydrogen gas moved more rapidly into the cylinder than the air inside could move out, and hence an excess of pressure quickly arose in the interior.

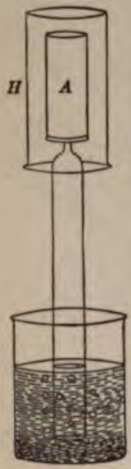


Fig. 30.

Exact measurement shows that the lighter a gas is in bulk, the faster its parts move by diffusion in any direction. The rate is inversely proportional to the square root of the density of the gas. Thus, for hydrogen and air it is in the ratio $\sqrt{1.293} : \sqrt{0.0897}$, or 3.8 : 1.

Chemical Properties. — Hydrogen, delivered from a jet, burns in air or pure oxygen. A cold vessel held over the almost invisible blue flame condenses to droplets of water the steam that is produced (Fig. 31). When hydrogen and oxygen are mingled in a suitable burner (Fig. 32), although the flame gives little light, it is exceedingly hot. Platinum melts in it easily and an iron wire burns brilliantly. In a closed space it produces a temperature of over 2500°. When the flame is allowed to play on a piece of quicklime, the latter becomes white-hot at the spot where the flame meets it. This result is called a **calcium light** or **lime light.**

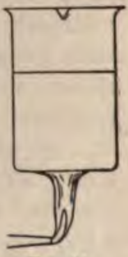


Fig. 31.

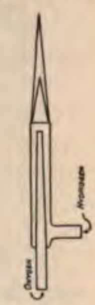


Fig. 32.

When hydrogen and oxygen are mixed, the chemical action is very slow at ordinary temperatures, *no perceptible amount of union occurring in a period of five years.* If the mixture is sealed up and kept at 300°, after several days a small part is found to have combined to form water. At 518°, hours are required before the union is complete. At 700° the combination is almost instantaneous. Hence contact with a body at a bright-red heat is required actually to explode the mixture.

Finely divided platinum, when held in the cold mixture, hastens the union (otherwise vanishingly slow) in the part of the gases in contact with it. The heat of the union raises the temperature of the platinum and of neighboring portions of the gas and causes explosion of the mass. The platinum is simply a contact agent (p. 29) and remains itself unaffected.

Hydrogen unites directly with a minority only of the simple substances. It combines rapidly with oxygen, chlorine, fluorine, and lithium, and more slowly with a few others.

Hydrogen acts also upon some of the compounds of metals with oxygen or chlorine. Thus, when any one of the oxides of iron is heated in a tube through which hydrogen flows, the latter combines with the oxygen to form water, and the metal is liberated. The skeleton equation (p. 51) is: $Fe_3O_4 + H \rightarrow H_2O + Fe$. We then reason that Fe_3 will give 3Fe. Since all the oxygen is removed from the compound, O_4 will give $4H_2O$. To produce this, 8H is required. Hence:

$$Fe_3O_4 + 8H \rightarrow 4H_2O + 3Fe.$$

This interaction is classed as a displacement. In describing it the chemist would also say that the hydrogen has been *oxidized* and that the oxide of the metal has been *reduced* (pp. 36–37).

The Order of Activity of the Metals. — We employ metals so frequently in chemistry, that we must at once become familiar with the key to the main differences in their behavior. The order of their activity explains these differences, as well as many other facts. In the adjoining list, the most active metals are at the top. Hydrogen is not a metal, but is included because chemically it resembles the metals. All the metals above hydrogen displace this element from dilute acids (and from water), while those below it do not.

The first displaces the hydrogen from water violently, the second less vigorously. Magnesium barely acts on boiling water, but, like iron, acts on superheated steam. Zinc liberates hydrogen with reasonable vigor from dilute acids, lead rather feebly, and copper and those following not at all.

ORDER OF ACTIVITY.
METALS

Potassium
Sodium
Calcium
Magnesium
Aluminium
Manganese
Zinc
Chromium
Iron
Nickel
Tin
Lead
Hydrogen
Copper
Bismuth
Antimony
Mercury
Silver
Platinum
Gold

Other facts are explained by the table. Thus, when the metals are heated in pure oxygen, the last two do not combine. Those above silver do unite with oxygen — mercury rather slowly and the others more and more energetically as we ascend the list. Again, if we take the oxides of the metals, we find that those of the metals up to and including mercury lose all their oxygen when heated. If we heat the oxides, and lead hydrogen over them, the oxygen is easily removed from all the oxides up to and including those of iron, leaving in each case the metal. Thus, in general, the more active metals form the most stable compounds.

The metals following hydrogen are the ones which are found in nature in large amounts in the free condition.

Exercises. — 1. Make equations for reactions in which hydrogen is liberated by the action of: (*a*) hydrochloric acid and magnesium giving $MgCl_2$, (*b*) steam and zinc giving ZnO.

2. Make an equation for the action of heat on manganese dioxide MnO_2 giving oxygen and Mn_3O_4.

CHAPTER VI

VALENCE. CALCULATIONS

Equivalence and Valence.—If the equations showing displacement of hydrogen by a metal be now re-examined, a peculiarity will be observed which we have thus far omitted to note. When sodium (p. 50) and calcium (p. 51) act upon water, one atomic weight (or atom) of the former displaces one atomic weight of hydrogen, but one atomic weight of the latter displaces twice as much hydrogen. Again, one atom of zinc (p. 53) displaces two atoms of hydrogen, but one atom of aluminium displaces three. Assuming, for simplicity, that we allow three of these metals all to act upon dilute hydrochloric acid, the equations are:

$$Na + HCl \rightarrow NaCl + H.$$
$$Ca + 2HCl \rightarrow CaCl_2 + 2H.$$
$$Al + 3HCl \rightarrow AlCl_3 + 3H.$$

Interpreting this, we perceive that the atom of aluminium, for example, displaces 3H, *because it is able to combine with 3Cl,* and so incidentally liberates the hydrogen formerly united with 3Cl. The atom of sodium, however, can unite with only 1Cl, and so releases only 1H. Now this is not a rule confined to these reactions, but represents a general chemical property of the atomic weight of each element, and a property which we shall find most useful.

The atom of aluminium releases 3H because it can take the place of three atoms of hydrogen in chemical combination (and hold 3Cl). The atomic weight of aluminium is said to be *equivalent to* (equal in chemical value to) three atomic weights of hydrogen. Since it combines with 3 atomic weights of chlorine, it is also considered to be equi-valent to 3 atomic weights of this element.

The *chemical property* referred to is called **valence.** The valence of an atomic weight of hydrogen or of chlorine is the unit. An atomic weight of sodium is said to be **univalent,** one of calcium

bivalent, one of aluminium **trivalent.** The formula H_2O shows the atomic weight of oxygen to be bivalent, because it unites with two atomic weights of hydrogen. Apparently, the atomic weight (or atom) of each element has a fixed capacity for combining with not more than a certain number of atomic weights (or atoms) of other elements.

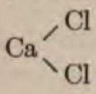
Marking the Valence. — Until we have become familiar with the valence of each element, it is advisable to mark the valences in a special way: Na^{I}, Ca^{II}, Al^{III}, O^{II}, Zn^{II}, Cl^{I}.

As we should expect, a bivalent atom can combine with two univalent atoms, *or with one bivalent atom,* and so forth. Thus we have the compounds of oxygen: $Na_2{}^{I}O^{II}$, $Ca^{II}O^{II}$, $Al_2{}^{III}O_3{}^{II}$, $Zn^{II}O^{II}$, $Cl_2{}^{I}O^{II}$.

The rule is that the quantities of two elements which combine must have equal total combining capacities — *i.e.*, identical total valence. Thus, Ca^{II} has the valence two, and so does O^{II}. Again, $Al_2{}^{III}$ has a total valence of 2×3 (=6) and so has $O_3{}^{II}$ ($3 \times 2 = 6$).

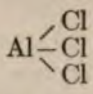
Frequently the valence is marked by means of lines, the number of lines pointing towards a symbol indicating the valence of the atom it represents:

$Na-Cl$



$Ca\begin{matrix}/Cl\\ \backslash Cl\end{matrix}$

$Ca=O$



$Al\begin{matrix}/Cl\\ -Cl\\ \backslash Cl\end{matrix}$

$O=Al-O-Al=O$

Definition. — The **valence of an element** is **a number representing the capacity of its atomic weight to combine with, or displace, atomic weights of other elements, the unit of such capacity being that of one atomic weight of hydrogen or chlorine.**

Valence of Radicals. — What we have said applies to compounds of not more than two elements — so called **binary compounds.** We cannot with certainty tell the valences in a compound of three or more elements, like H_2SO_4. But we have seen that the acids behave as if composed of two radicals: H(Cl), $H_2(SO_4)$, that is, of two groups which move as wholes in chemical reactions. Hence we can assign a valence to a compound radical *as a whole.* Thus, $(SO_4)^{II}$ is evidently bivalent, as a whole, because it is united with $2H^{I}$. Na(OH) and $Ca(OH)_2$ show the radical **hydroxyl** (OH) to be univalent.

It is to preserve the identity of the radicals, and to make them easily recognizable, that we write them in brackets and place the coefficient outside, as $Ca(OH)_2$ and $Al_2(SO_4)_3$, instead of using the forms CaO_2H_2, $Al_2S_3O_{12}$, and so forth. In fact, substances which commonly interact as if the radicals were single elements, we regard as binary compounds.

In writing formulæ of inorganic compounds we usually place the positive radical (p. 53) in front and the negative radical after it.

Use in Making Formulæ and Equations. — The chief use of the conception of valence is the very practical one of enabling us to write formulæ. In making equations we constantly need to know whether the chloride of an element, say magnesium, is $MgCl$, or $MgCl_2$, or $MgCl_3$, or $MgCl_4$, etc., and whether its sulphate is $MgSO_4$, or Mg_2SO_4, or some other combination of the symbols. To answer questions like this it is not necessary to know the formula of every compound of each element; the apparent disorder of these numbers can be reduced to rule, and the reader should endeavor thoroughly to master the rule before going farther.

Thus, suppose that we require the formula of aluminium hydroxide. Up to this point, we should have been compelled to look for it in a book. And if, later, we needed the formula of aluminium sulphate, we should have had to look that up, separately, also. But now, all we need is to know the valence of aluminium Al^{III}, of the hydroxyl radical $(OH)^{I}$ and of the sulphate radical $(SO_4)^{II}$. Making the total valences in the two halves of each compound alike, we write the formulæ $Al^{III}(OH)_3{}^{I}$, $Al_2{}^{III}(SO_4)_3{}^{II}$.

The reader must make a special effort to note the valences of each element and radical, and always to use them in making formulæ. If a formula is written from memory, the valences must be checked, to make sure that the formula is correct.

How to Learn the Valence of an Element. — To find out the valence of an element, we must obtain the formula of one simple compound of the element, containing another element of known valence. Thus, what is the valence of carbon? Its oxide is CO_2. The total valence of oxygen here is $2 \times 2 = 4$. Carbon C^{IV} is therefore quadrivalent. Hence its chloride must be $C^{IV}Cl_4^{I}$ (carbon tetrachloride), and it should give a compound with hydrogen $C^{IV}H_4^{I}$ (methane, composing a large part of natural gas). When carbon combines with a trivalent element, equi-valent amounts of each element must be used, as in $Al_4^{III}C_3^{IV}$ (aluminium carbide), where Al_4^{III} and C_3^{IV} contain 3 × 4, or 12 units of valence each.

The chemist does not memorize the valences themselves; he **recovers the valence of an element or radical, when needed, by recalling the formula of a substance containing this element or radical in combination with a more familiar element or radical,** such as Cl^{I} or H^{I}.

Elements with More than One Valence. — The rule of valence is somewhat complicated by the fact that many elements show more than one valence. In other words, the combining capacity of an atomic weight of such an element may have two (or even more) values, according to the conditions under which the action takes place.

Thus, we have encountered two chlorides of iron, ferrous chloride $Fe^{II}Cl_2^{I}$ and ferric chloride $Fe^{III}Cl_3^{I}$. We have, in fact, two complete series of compounds of iron, such as:

Bivalent (Ferrous): $FeCl_2$, FeO, $FeSO_4$.
Trivalent (Ferric): $FeCl_3$, Fe_2O_3, $Fe_2(SO_4)_3$.

When an element forms two such series of compounds, we always call particular attention to the fact.

Exceptional Valences. — Some elements show an exceptional valence in one compound. The valences shown in series of compounds are the important ones, and the exceptions need not particularly concern us. Thus, in addition to the oxides FeO and Fe_2O_3, iron gives the magnetic oxide Fe_3O_4, where the valence of iron appears not to be a whole number, but $\frac{8}{3}$ or $2\frac{2}{3}$. Hence the valence is made regular by supposing the oxide to be a compound of the other two oxides, as if the formula were $Fe^{II}O,Fe_2^{III}O_3$.

Nomenclature. — The names of compounds containing only two elements (the true binary compounds) end in **ide**. Such are the ox*ides*, as ferric ox*ide* Fe_2O_3; the carb*ides*, as aluminium car-

bide Al_4C_3; the chlor*ides*, as sodium chlor*ide* NaCl; the sulph*ides*, as ferrous sulph*ide* FeS, etc.

When an element forms two (or more) compounds with another element, they are frequently distinguished thus: carbon *di*oxide CO_2, carbon *mon*oxide CO; phosphorus *pent*oxide P_2O_5, phosphorus *tri*oxide P_2O_3.

To distinguish two compounds of the same elements, another plan is also used: ferr*ous* chloride $FeCl_2$, ferr*ic* chloride $FeCl_3$; mercur*ous* oxide Hg_2O, mercur*ic* oxide HgO. The suffix *ous* indicates that the metal is combined with the smaller proportion of the negative element, and *ic* that it is combined with the larger proportion.

The tendency — although not a universal rule — is to use the latter plan with compounds containing a metal and the former with compounds containing only non-metals.

Equivalent Weights. — In the foregoing discussion of valence, we have more than once used the word "equivalent." For example (p. 61), it was stated that the atomic weight of aluminium is *equivalent* to three atomic weights of hydrogen, because it displaces them, and to three atomic weights of chlorine, because it combines with that number:

$$\begin{array}{lccccccc} & Al & + & 3HCl & \rightarrow & AlCl_3 & + & 3H \\ \textit{Weights:} & 27.1 & & 3 \times 36.468 & & 27.1 + 3 \times 35.46 & & 3 \times 1.008 \end{array}$$

Now chemists often view this from the other direction, and say that 1.008 g. of hydrogen are displaced by 9.03 g. of aluminium (one-third of the atomic weight) and that 35.46 g. of chlorine combine with only 9.03 g. of aluminium. When taking this view, they refer to **the weight of an element displacing one atomic weight of hydrogen,** or **combining with one atomic weight of chlorine** (or of any other univalent element) as the **equivalent weight of that element.** The equivalent weight of aluminium is therefore 9.03 and that of calcium Ca^{II} 20 (one-half the atomic weight) and that of sodium Na^{I} 23 (the atomic weight).

It will be seen that the equivalent weight can always be found by a quantitative experiment. It is also evident that it is equal to the atomic weight divided by the valence. It is likewise clear that the equivalent weight of an element, multiplied by the valence of that element, is equal to the atomic weight. The conception of equivalent weights finds application in several connections in chemistry (see Normal Solutions and Faraday's Law).

CALCULATIONS

As we have seen (p. 44), the formula represents the composition of a substance, using the atomic weights as the units. We have learned how the formula is calculated from measurements made in an experiment (p. 45). We may now take up some of the ways of using the information contained in a formula.

Composition from the Formula. Formula-Weight. — To learn the composition of a substance, such as potassium chlorate, $KClO_3$, from its formula, we look up the values of the atomic weights (inside rear cover). We find $K = 39.1$ parts of potassium, $Cl = 35.46$ parts of chlorine, and $O_3 = 3 \times 16.00$ or 48 parts of oxygen. The proportions, in order, are therefore: $39.1 : 35.46 : 48$.

What is the proportion of oxygen to potassium and chlorine, together? It is $48 : 39.1 + 35.46$, or $48 : 74.56$, or $1 : 1.55$.

We require a name for the sum of the weights of the constituents indicated in the formula. This is called the **formula-weight.** Thus, for potassium chlorate, it is $39.1 + 35.46 + 48$, or 122.56.

To Find the Percentage Composition. — In potassium chlorate the proportions are 39.1 of potassium, 35.46 of chlorine, and 48 of oxygen or a total of 122.56. In one hundred parts, the potassium is $\frac{39.1}{122.56} \times 100$, or 31.9%; the chlorine $\frac{35.46}{122.56} \times 100$, or 28.9%; and the oxygen $\frac{48}{122.56} \times 100$, or 39.1%.

Stated in terms of the rule of proportion, we have, for the potassium, $122.56 : 39.1 :: 100 : x$, where x is the percentage of potassium.

Calculations by Use of Equations. — We frequently wish to know what weight of a product can be obtained from a given weight of the necessary materials. For example, what weight of ferrous sulphide can be made with 100 g. of iron? It is understood that the necessary sulphur is available.

To avoid the blunders which are easily made, observe strictly the following rules:

1. **Write down the equation:**

$$\mathrm{Fe} + \mathrm{S} \rightarrow \mathrm{FeS}.$$

2. **Place under each formula the weight it represents:**

$$\begin{array}{ccccc} \mathrm{Fe} & + & \mathrm{S} & \rightarrow & \mathrm{FeS} \\ 55.84 & & 32.06 & & 87.90 \end{array}$$

3. **Read this expanded equation.** In this case it reads: 55.84 parts of iron combine with 32.06 parts of sulphur to give 87.90 parts of ferrous sulphide.

4. **Re-read the original problem:** "What weight of ferrous sulphide can be made with 100 g. of iron?" Having done this, place the amount given in the problem (100 g. of iron) under the formula of the substance in question. Then notice what the problem asks ("what weight of ferrous sulphide") and place an x under the formula of that substance:

$$\begin{array}{ccccc} \mathrm{Fe} & + & \mathrm{S} & \rightarrow & \mathrm{FeS} \\ 55.84 & & 32.06 & & 87.90 \\ 100\text{ g.} & & & & x \end{array}$$

5. **Read the problem as now tabulated:** 55.84 g. of iron give 87.90 g. of ferrous sulphide, therefore 100 g. of iron will give x g. of ferrous sulphide.

6. **State the proportion in this order** (or, see below).

$$55.84 : 87.90 :: 100 : x\ (=157.4\text{ g}).$$

If the tabulation in rule 4 has been prepared correctly, this final statement as a proportion is purely mechanical. It will be noted that only two of the three quantities given in the expanded equation were actually used.

6a. **Alternative Method.** At the sixth step, we may also say: If 55.84 g. of iron give 87.90 g. of ferrous sulphide, 1 g. of iron will give $\frac{87.90}{55.84}$ g. (= 1.574 g.) of ferrous sulphide. Then, if 1 g. of iron gives 1.574 g. of ferrous sulphide, the 100 g. of iron will give 100 × 1.574 g. (= 157.4 g.) of ferrous sulphide.

Warnings. — In solving the exercises at the end of the chapter, beware of three kinds of mistakes, which are commonly made.

1. Do not read the problem carelessly and make the equation backwards, that is, with the sides reversed. Focus attention first on the exact chemical change involved.

2. Do not speak, or think of the symbols Fe and S as standing for "1 part" of iron or sulphur. They stand for 1 *chemical* unit, or atomic weight, or atom, in each case, that is, for "55.84 parts" and "32.06 parts," respectively.

3. Follow the rules laid down above. The chemist follows these rules. The beginner always thinks he can do without them, and he fails in consequence. Writing the equation in expanded form (rule 4) and reading the problem into it (rule 5) are absolutely essential steps.

Another Example. — What weight of hydrogen is required to reduce 45 g. of magnetic oxide of iron to metallic iron?

Following the rules, as before, we reach the expanded equation:

$$\begin{array}{ccccccc}
Fe_3O_4 & + & 4H_2 & \rightarrow & 3Fe & + & 4H_2O. \\
3 \times 55.84 + 4 \times 16 & & 8 \times 1.008 & & 3 \times 55.84 & & 4(2 \times 1.008 + 16) \\
167.52 + 64 & & 8.064 & & 167.52 & & 4 \times 18.016 \\
231.52 & & 8.064 & & 167.52 & & 72.064 \\
45 \text{ g.} & & x & & & &
\end{array}$$

Observe that the atomic weights are multiplied by the subnumbers, so that, for example, $Fe_3 = 3 \times 55.84$. Observe also that the formula-weights are multiplied by the coefficients, when such occur in front of the formulæ, so that, for example, $4H_2O = 4 \times 18.016$.

The proportion $231.52 : 8.064 :: 45 : x$ $(= 1.57)$ supplies the answer, 1.57 grams of hydrogen.

Using the alternative plan: If 231.52 g. of magnetic oxide are reduced by 8.064 g. of hydrogen, 1 g. will be reduced by $\frac{8.064}{231.52}$ g. $(= 0.035$ g.) of hydrogen. Hence, if 1 g. of magnetic oxide is reduced by 0.035 g. of hydrogen, 45 g. will be reduced by 45×0.035 g. $(= 1.57$ g.) of hydrogen.

Exercises. — 1. What are the valences of the negative radicals of phosphoric acid H_3PO_4, and of acetic acid (p. 52)? What must be the formulæ of calcium phosphate, cupric acetate (Cu^{II}), aluminium phosphate, ferrous carbonate ($CO_3{}^{II}$), ferrous sulphate, cupric chloride?

2. What is the valence of phosphorus in phosphorus pentoxide (p. 32)? What must be the formulæ of, (*a*) the corresponding chloride and sulphide of phosphorus, and (*b*) of aluminium oxide?

3. What are the valences of the elements in the following: LiH, NH_3, SeH_2, BN?

4. What are the valences of the metals and radicals in the following: HNO_3, $Pb(NO_3)_2$, $Ce(SO_4)_2$, KCl, $KMnO_4$ (potassium permanganate)? Name all the substances in 3 and 4.

5. Make equations to represent, (*a*) the reduction of lead dioxide (PbO_2) by hydrogen, (*b*) the actions of aluminium upon cold water and, (*c*) upon steam at a red heat.

6. What weight of mercury is obtained from 120 g. of mercuric oxide HgO?

7. What weight of mercuric oxide will furnish 20 g. of oxygen?

8. What weight of Fe_2O_3 may be obtained from 10 g. of oxygen?

9. How much silver is contained in 100 g. of an impure specimen of silver chloride AgCl which is 33 per cent sand?

10. What are the percentage compositions of cerium sulphate $Ce(SO_4)_2$, phosphorus pentachloride PCl_5, and ammonium chloride NH_4Cl?

11. What weight of hydrogen is required to reduce 100 g. of ferric chloride $FeCl_3$ to ferrous chloride $FeCl_2$?

CHAPTER VII

THE MEASUREMENT OF QUANTITY IN GASES. RELATIONS BETWEEN STRUCTURE AND BEHAVIOR OF MATTER

A SPECIMEN of a gas, like a specimen of a solid or a liquid, may be weighed, but it is usually easier to determine the quantity of the gas by (1) measuring its volume, and at the same time (2) noting its temperature on a thermometer suspended in it or close to it, and (3) ascertaining the pressure which it exercises.

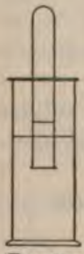


FIG. 33.

The Measurement of the Pressure of a Gas. — In almost all cases the easiest way to take account of the pressure of a gas is to place it in an apparatus so constructed that one boundary of the volume is a liquid. The apparatus is then so adjusted that the surface of the liquid in contact with the gas in the closed tube (Fig. 33) is *at the same level* as the *free* surface of the liquid which is exposed to the atmosphere. The equality in the levels of the liquids is then a guarantee that the specimen of gas and the atmosphere are exercising equal pressures on the liquid. At this stage the volume of the gas is measured, by reading the graduation (not shown) on the tube. Simultaneously the pressure of the atmosphere and, therefore, of the gas, is ascertained by reading the barometer.

The barometer (Fig. 34) consists of a bent tube containing mercury. The short limb (to the left) is open and the pressure of the atmosphere is exercised on the surface of the mercury there. The longer limb (to the right) is closed at the top and in it there is no gas above the mercury. When the tube is inclined, the surface of the mercury in the longer limb endeavors to retain the same vertical height above the lower surface and consequently rises and, with sufficient inclination, will reach entirely to the top of the tube. The downward pressure of the mercury on the right, above the tly equal to the pressure of the atmosphere on the cury at the same level. The amount of the onal to the length of the column of mer- Hence, reading the ds above the free ressure of the which is

is uld rcury ing the eter and ading the rrections, *C*,

us, after adjust- 200 c.c. and its rrected barometric barometer (perhaps the gas) at 15°. The The corrected reading is

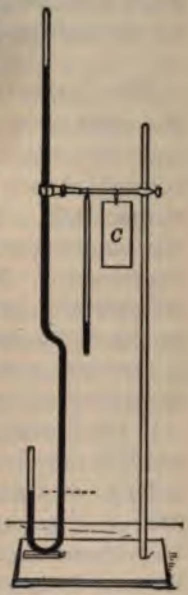


FIG. 34.

the *Volume to 760 mm. Pressure.*— atmospheric pressure varies from day to day, the observed pressure is corrected to that which the of gas would have occupied at the standard pressure of mercury. By careful measurements, **Boyle** (1660) the **volume occupied by the same sample of any gas** **versely with the pressure.**

illustration just given will show how this additional correc- applied. There were 200 c.c. of the gas at 17° and 742 mm. The question is: What would be the volume of this amount of gas at 760 mm.? At this new pressure (760 mm.), which is *greater* than the old pressure (742 mm.), the volume will become *less*. Hence we change the volume in the proportion of these pressures, *placing the smaller number in the numerator*, so as to get a smaller volume as the answer: 200 × $\frac{742}{760}$ = volume at 760 mm.,

= 195.3 c.c. If we wished to convert 100 c.c. at 775 mm. to 760 mm., we should reason that the new pressure was smaller, and the volume would become greater, and should therefore place the larger number (775) in the numerator so as to get a larger volume for the answer.

The Correction of the Volume of a Gas for Temperature.— The same sample of gas will occupy, when heated, a larger volume, and when cooled, a smaller volume than before. The change in volume for each degree Centigrade is $\frac{1}{273}$ of the volume of the same sample at 0°. To simplify the calculation we begin by converting the temperature to the absolute scale by adding 273° to each temperature. **The volumes assumed by a sample of gas at different temperatures, the pressure remaining constant, are in the same proportion as the corresponding absolute temperatures** (**Charles**, 1787). If the volume remains constant, then the pressure changes in the same proportion.

In the illustration used above, there were 200 c.c. of gas at 17°, and it is required to know the volume at 0°. We *add 273 algebraically to each temperature*, and the question becomes: There are 200 c.c. of gas at 290° Abs., what will be its volume at 273° Abs.? The volume changes in the direct ratio of the absolute temperatures. The new temperature is *lower* than the old, and the new volume will therefore be *smaller* than the old. Then $200 \times \frac{273}{290}$ = volume at 0° (273° Abs.) = 188.3 c.c.

The above laws are usually applied to any example simultaneously. Thus, 200 c.c. of gas at 742 mm. pressure (corr.) and 17° become $200 \times \frac{742}{760} \times \frac{273}{290} = 183.8$ c.c. at 0° and 760 mm.

Mixed Gases: Aqueous Tension. — Two gases at the same temperature, provided they do not interact chemically, do not interfere with each other's pressures when mixed. Thus, if they are forced into the same volume, the pressure of the mixture is equal to the sum of those of the components (Dalton's law, 1807). The gases are therefore still thought of individually, and the share which each gas has in the total pressure is called its **partial pressure.** This, like any other gaseous pressure, is proportional to the concentration of the particular gas in the mixture.

For example, a gas measured over water contains water vapor.

The partial pressure of this, called **aqueous tension** (*q.v.*), which is definite for each temperature, must be subtracted from the total pressure. The remainder is the partial pressure of the gas being measured, and this remainder is used as the pressure of this gas in any calculation. Thus, in a gas measured over water at 22°, the total pressure includes 19.7 mm. pressure of water vapor (the aqueous tension at 22°, see Appendix IV). Hence 150 c.c. of gas over water at 22° and 750 mm. is the same in amount as 150 c.c. of the same gas in dry condition at 22° and 730.3 mm. (there being simply 150 c.c. of water vapor at 19.7 mm. mixed with it). To obtain the volume of dry gas at 0° and 760 mm. we have the expression $150 \times \frac{273}{295} \times \frac{730.3}{760}$.

Densities of Gases.*[*]* — The **density** of a gas is the mass **of 1 c.c. of the gas** at 0° and 760 mm. pressure. Sometimes the weight of one liter (1000 c.c.) is called the density. Often the *relative* weight of the gas, the weight of an equal volume of air, or oxygen, or hydrogen being taken as unity, receives the same name.

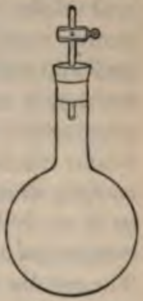


FIG. 35.

The most direct method of measuring the density of a gas is to employ a light flask of 125–150 c.c. capacity, provided with a rubber stopper and stopcock (Fig. 35). By means of an air-pump the contents of the flask are removed, and it is weighed. This gives the weight of the empty vessel. The gas, whose density is to be ascertained, is then admitted, and care is taken that it finally fills the flask at the pressure of the atmosphere. The flask is closed and weighed again. The increase represents the weight of the gas. At the same time the temperature and barometric pressure are read. The volume is determined by displacing the gas once more from the flask, filling with water, and weighing again. The difference in weight between the empty flask and the flask full of water, in grams, represents the volume of the content of the flask in cubic centimeters. This volume is reduced to 0° and 760 mm. by the rules discussed above, and we have then a volume of the gas and the corresponding weight.

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[*] The subjects of this section are not actually used until Chapter IX (on Molar Weights) is reached.

To illustrate, let us suppose that the volume of the flask is 200 c.c. and that it is filled with oxygen at 17° and 742 mm. The weight of the gas is found to be 0.26 g. We ascertained (p. 72) by calculation that at 0° and 760 mm. this volume would be 183.8 c.c. The weight of a liter is given by the proportion 183.8 : 0.26 :: 1000 : x. Here $x = 1.415$ g. When the operation is performed carefully, and the weighing carried to the nearest milligram instead of the nearest centigram, a result more nearly approaching the accepted one (1.429) may easily be reached.

To get the density of oxygen referred to hydrogen as unity, we must divide the answer by the weight of a liter of hydrogen (0.08987 g.). In the above case the quotient is 15.74. The accepted value is 15.90. The density referred to air as unity is similarly obtained by dividing by 1.293, the weight of a liter of air at 0° and 760 mm. pressure.

By using a modification of the flask just described, it is possible to ascertain the weights of known volumes of the vapors of liquids and solids. A temperature sufficiently high to vaporize the substance must be employed. The volume is reduced by rule to 0° and 760 mm. and the density (in this case known as the **vapor density**) is calculated as before. The reduction to 0° and 760 mm. pressure by rule gives, of course, a fictitious result. The vapor would condense to the liquid form before 0° was reached, if the cooling were actually carried out. But the value for the density *as it would be* at 0° and 760 mm. has to be calculated to facilitate comparison with the corresponding values for other substances. The results have no physical significance, but are highly important to the chemist.

RELATIONS BETWEEN THE STRUCTURE AND BEHAVIOR OF MATTER

We have seen that matter is composed of minute particles called molecules. Just as we can thoroughly understand the behavior of a watch or an automobile engine only if we know the details of its structure, and how the parts work, so we can understand the physical and chemical behavior of matter in masses only if we are familiar with its ultimate mechanism. Hence, we must now take up the structure of matter in its three states, the gaseous, the liquid, and the solid. In doing this, we shall keep constantly in view the connection between the molecular relations and the general behavior of the matter.

The Molecular Structure of Gases. — The most noticeable fact about gases is that they *can be compressed* to an enormous extent. Oxygen at 760 mm., for example, can be reduced by pressure to one two-hundredth of its volume, or even less. The compression does not affect the individual molecules, and therefore does not diminish the volume actually occupied by the oxygen, but it crowds the molecules closer together and **diminishes** to one two-hundredth **the space** between them. Compressing a gas is, in fact, mainly compressing the *empty space* of which it chiefly consists. To understand what follows, the reader must keep constantly before him a mental image of a jar of gas as consisting of small particles separated by relatively wide, empty spaces. The molecules are in rapid motion and move in straight lines, excepting when they strike one another or the walls of the vessel.

The Properties of Gases. — Let us now note the more obvious qualities of gases, printing in *italics* the *fact concerning a mass of gas* and in **black type** the property of the molecules which accounts for the fact.

The most remarkable thing about a gas, considering the looseness with which its material is packed, is the total *absence* in it *of any tendency to settling* or subsidence. Since the molecules cannot be at rest upon one another, as the great *compressibility* shows, we are driven to conclude that they are **widely separated from one another,** and that they occupy the space, otherwise a complete vacuum, by **constantly moving about in all directions.** But a moving aggregate of particles which does not even finally settle must be in perpetual motion. We must, therefore, believe the molecules to be wholly unlike particles of matter in having **perfect elasticity,** in consequence of which they undergo no loss of energy after a collision. They must continually strike the walls of the vessel and one another and rebound, yet without loss of motion. The fact that each gas is *homogeneous*, efforts to sift out lighter or heavier samples having failed, requires the supposition that **all the molecules** of a pure gas are **closely alike.**

The *diffusibility* of gases is due to the **motion of the molecules,** and their *permeability* to the **space** available to receive molecules of another gas. These two modes of behavior involve no additional molecular properties. The word "diffusion" is often thought to mean the property of a given mass of gas in virtue of which another gas can mix with the given mass. This property is not diffusibility but permeability. It is the other gas, which makes its way into the given gas, which is diffusing. Diffusion is spontaneous motion of the parts of a gas *away from* their original location. Unless this motion is into an empty space, the diffusing molecules must, of course, move into another body of gas. In the case of the jars of hydrogen and air (p. 57), each gas moved in part *out of* its original jar (diffused), and each received parts of the other gas *into* its jar (was permeated).

Boyle's Law and Charles' Law. — Passing now to *Boyle's law* (p. 71), the thing to be accounted for is that when a sample of a gas diminishes in volume, its pressure increases in the same proportion. Let the diagram (Fig. 36) represent a cylinder with a movable piston, upon which weights may be placed to resist the pressure. Now the pressure exercised by the gas under the piston cannot be like the pressure of the hand upon a table, since we have just assumed that the particles are not even approximately at rest, and the spaces between them are enormous compared with the size of the molecules themselves. The gaseous pressure must therefore be attributed to the colossal hailstorm which their innumerable impacts upon the piston produce. If this is the case, the compressing of a gas must consist simply in moving the partition downwards, so that the particles as they fly about are gradually restricted to a smaller and smaller space. Their paths become on an average shorter and shorter. Their impacts upon the walls become more and more frequent. So the pressure which this causes becomes greater and greater, and is proportional to the degree of crowding (the **concentration**) of the molecules.

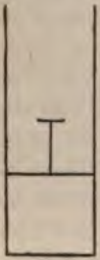
FIG. 36.

There are two other points to be added. When we diminish the volume to one-half, we find from experience that the pressure becomes exactly, or almost exactly, twice as great. This must mean that, although the particles are becoming crowded, they do not interfere with one another's motion, excepting of course where actual collision causes a rebound. Only in the absence of interference would doubling the number of molecules per unit of volume give exactly double the number of impacts on the walls. Hence the molecules must have practically no tendency to cohesion. Finally, the molecules must be supposed to move in straight lines between collisions.

A baseless idea, that the molecules of a gas repel one another, still lingers in some quarters. There is no evidence of this. The molecules pay almost no attention to one another, either by attraction or repulsion.

Boyle's law therefore adds four more details concerning molecular behavior, namely, that the **impacts of the particles** produce the *pressure*, that the **crowding of the molecules** represents the *concentration of the material* and that the particles **move in straight lines** and **show almost no cohesion,** since *pressure* and *concentration are very closely proportional to one another.*

How, now, can we account for *Charles' law* (p. 72), according to which an increase in pressure (or in volume) results from heating a mass of rapidly moving molecules? The action of a particle colliding with a surface is measured in physics in terms of its mass and its velocity. It is evident that *heating* a cloud of molecules would not increase the mass of each, and it must therefore **increase the velocity of each,** since the kinetic energy of all becomes greater.

Avogadro's Law. — The identical general behavior of all kinds of gases suggests that their structures may be all alike. Avogadro (1811), the professor of physics in Turin, put forward the hypothesis that the numbers of molecules in equal volumes of different gases, at the same temperature and pressure, might be equal. A more strict study of the properties we have been considering, and of some additional facts, has since shown that no other conjecture than Avogadro's would be consistent with them. Thus it is now accepted as a fact, and is known as **Avogadro's law.** It may also be put in the form: **At the same temperature and pressure, the molecular concentration of all kinds of gases has the same value.**

Diffusion. — The *law of diffusion* (p. 58) harmonizes with the conceptions of molecular structure without further additions to the latter. The speed of the hydrogen molecule at room temperature is 1840 meters per second. The masses of the oxygen and hydrogen molecules are as 16 : 1, and the speeds of diffusion (p. 58) as $\sqrt{1} : \sqrt{16}$, or 1 : 4. Hence the speed of the oxygen molecule is one-fourth of 1840, or 460 m. per sec.

Calculation shows the activity of the molecules to be such that, in air, the number striking a single square centimeter of surface per second would fill no less than twenty liters.

Liquefaction of Gases: Critical Temperature. — Finally, gases can be *liquefied by sufficient cooling and compression.* This fact compels us to suppose that, after all, even gaseous molecules have a tendency to **cohesion.** This cohesion is scarcely perceptible so long as the gas is warm and is diffuse. Thus, 2 liters of oxygen at 1 atmosphere pressure, when subjected to 2 atmospheres pressure, give 0.9991 liters instead of 1 liter. The additional contraction of 0.0009 liters (0.9 c.c.) is due to the effect of cohesion when the molecules are thus crowded closer together. The gases which are more easily liquefied than is oxygen show greater effects. Thus, 2 liters of sulphur dioxide at 760 mm., when subjected to 2 atmospheres pressure, give only 0.974 liters, showing a contraction due to cohesion of 26 c.c. These data refer to 0°. At lower temperatures the contractions due to cohesion become rapidly greater. This cohesion is not of the nature of gravitational attraction.

We can readily understand, therefore, that when the kinetic energy of the molecules is sufficiently reduced by cooling (namely, to, or below the critical temperature, see below), and the molecules are brought sufficiently close together, the tendency of the molecules to cohere causes the gas to condense and assume the liquid form. In 1869 Andrews found that carbon dioxide could be liquefied at 0° by 38 atmospheres pressure, and at 30° by 71 atmospheres, but that above 31.35° it could not be liquefied by any pressure. He discovered that each gas has a **critical temperature,** as he called it. For carbon dioxide, this temperature can be observed by placing a heavy-walled, glass tube (Fig. 37), half-filled with liquid carbon dioxide, in a beaker of water, and gradually raising the temperature of the latter. At 31.35°, the surface between the liquid and gas becomes hazy and vanishes. When the temperature falls once more, the surface re-appears at 31.35°. This shows that, with Faraday's "permanent" gases, a temperature below the critical point had not been employed.

The critical temperature of oxygen is −118°, of hydrogen −234°, of carbon dioxide 31.35°, of sulphur dioxide 156°, of water 358°.

Fig. 37.

Another Deviation from the Laws of Gases. A Perfect Gas. — It may be added that when a gas is already under very high pressure, and very closely packed, *an increase in the pressure does not produce quite as great a diminution in volume as Boyle's law leads us to expect.* This reminds us that we are **diminishing only the space between the molecules,** and not the volumes of the molecules themselves, and therefore not the total volume of the gas. When, on severe compression, the volume occupied by the molecules themselves has become an appreciable fraction of the whole volume, additional compression does not affect the whole volume, and the contraction is smaller than Boyle's law would indicate. Thus, 2 liters of hydrogen, even at one atmosphere pressure, when subjected to two atmospheres pressure, give 1.0006 liters, instead of 1 liter.

The last two effects (namely, those due to the tendency to cohesion of, and the space occupied by the molecules) are called **deviations** from the laws of gases. In consequence of these individual deviations, there are not *exactly* equal numbers of molecules in equal volumes of any two different gases, at the same temperature and pressure. An imaginary gas, which exhibits neither deviation, called a **perfect gas,** is often referred to in discussing the behavior of gases.

Summary. — We may now summarize the principal facts about gases in mass, appearing in italics above, with the corresponding features of the molecular relations, in heavy type, which we have added one by one.

Facts About Gases in Mass.	Corresponding Relations of Molecules.
Compressibility	Vacuum + molecules widely separated.
Diffusibility.	Molecules in rapid motion.
Permeability	Empty space relatively large.
Non-settling	Molecules perfectly elastic.
Homogeneity	Molecules of any one substance closely alike.
Pressure	Due to impacts of molecules.
Boyle's law	Pressure proportional to concentration of the molecules. Molecules move in straight lines and, when widely scattered, show no tendency to cohesion or to repulsion.
Charles' law.	Rise in temperature increases the velocity, and therefore the kinetic energy of the molecules.
Above and other facts .	Avogadro's law.
Law of diffusion . . .	....
Gases can be liquefied .	Molecules do possess a tendency to cohesion, which becomes conspicuous when they are cooled and closely crowded together.

History of the Kinetic Molecular Theory. — This theory was first suggested by Daniel Bernoulli (1738), who explained by its means the pressure and compressibility of gases. Lomonossov (1748) developed the theory very completely and by means of it explained Boyle's law and the effects of changes in temperature. He also anticipated from the theory the existence of the second deviation from the law of gases (1749), a discovery usually credited to Dupré (1864). He likewise pointed out that there was no limit to the maximum velocity of a molecule, and therefore no upper limit of temperature, but that there must be a lower limit (the absolute zero) at which the molecules would be at rest (1744). This work was entirely forgotten, until attention was called to it in 1904 by Menschutkin.

Similar views were expressed by Waterston (1845), but were still so much ahead of the time that the committee of the Royal Society did not approve the paper for publication, and it was discovered in the archives of the society, long afterwards, by Lord Rayleigh. The development of the theory, so far as it applies to heat, is therefore credited to Joule (1855–60) and, in respect to all properties of gases, to Krönig (1856) and Clausius (1857), who knew nothing of the earlier work.

Molecular Relations in Liquids. — The fact that even great pressures produce little diminution in the volume of a liquid shows that the free space, present in gases, is absent in liquids. The measured effects of various pressures show, for example in the case of water, that to reduce the volume to one-half would require, not doubling the pressure as in a gas, but increasing it from 1 to 10,000 atmospheres. The molecules of a liquid are actually in contact with one another.

The phenomena connected with surface tension, such as coherence into drops, show that cohesion plays a much larger part in liquids than in gases. On the other hand, liquids which are capable of mixing (*e.g.*, alcohol and water), when placed above one another in the same vessel, do mix, slowly, by diffusion. This indicates that motion of the molecules, although much impeded by friction, has not been annihilated by cohesion. The escape of vapor — that is, of part of the liquid in gaseous form — likewise proves that the molecules in the liquid are in motion. The relations of liquid and vapor can be discussed most effectively in the next chapter, in connection with the case of water and steam.

Molecular Relations in Solids. — The properties of solids differ from those of liquids chiefly in the fact that the solid has a definite form of which it can be deprived only with difficulty. This we may explain in accordance with the kinetic hypothesis by the supposition that the cohesion in solids is very much more prominent than in liquids. We obtain solids from liquids by cooling them; in other words, by diminishing the kinetic energy and therefore the velocity of the particles. The cohesive tendency of the latter is thus able to make itself felt to a greater extent. If, conversely, we heat a solid, or, according to the hypothesis, if we increase the speed with which the particles move, the body first melts and gives a liquid, and this finally boils and becomes a gas. The intrinsic cohesion of the particular substance can undergo no change, but the increasing kinetic energy of the particles steadily and continuously obliterates its effects. Yet some motion still survives in a solid. Thus we find that when the layer of silver is stripped from a very old piece of electroplate, the presence of this metal in the German silver or copper basis of the article is easily demonstrated.

The tendency of all solids to assume crystalline forms, which show definite cleavage and other evidences of **structure**, distinguishes them sharply from liquids. The force of cohesion in liquids is exercised equally in different directions. In solids it must differ in different directions in order that structure may result. Since each substance shows an individual structure of its own, these directive forces must have special values in magnitude and direction in each substance.

Crystallization. — A crystal arises by growth. When the process is watched, as it occurs in a melted solid or an evaporating solution, the slow and systematic addition of the material in lines and layers, as if according to a regular design, is one of the most beautiful and interesting of natural phenomena. The fern-like patterns produced by ice on a window-pane show the general appearance characteristic of crystallization in a thin layer. A larger mass in a deep vessel gives forms which are geometrically more perfect. From its very incipiency the crystal has the same form as when, later, its outlines can be distinguished by the eye. Hence the outward form is only an expression of a specific internal structure which the continual reproduction of the same outward form on a larger and larger scale leaves as a memorial of itself in the interior.

Crystal Forms. — Crystalline form is continually used in identifying (pp. 2, 12, 19) the substances produced in chemical actions. The classification of crystalline forms is carried out according to the degree of symmetry of the crystals:

1. Regular system.
2. Square prismatic system.
3. Hexagonal system.
4. Rhombic system.
5. Monosymmetric, or monoclinic system.
6. Asymmetric, or triclinic system.

The **regular system** presents the most symmetrical figures of all. Some forms which commonly occur are the octahedron (Fig. 38) shown by alum, the cube (Fig. 39) affected by common salt, and the dodecahedron (Fig. 40) frequently assumed by the garnet.

The **square prismatic system** includes less symmetrical forms than the previous one, since the crystals are lengthened in one direction.

Fig. 41 shows the condition in which zircon ($ZrSiO_4$), which furnishes us with the basis of certain incandescent illuminating arrangements, occurs in nature. The form of ordinary hydrated nickel sulphate ($NiSO_4,6H_2O$) is similar to this.

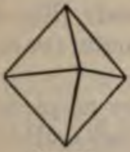

Fig. 38.

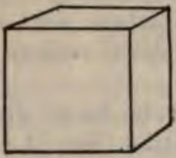

Fig. 39.

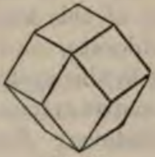

Fig. 40.

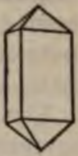

Fig. 41.

The **hexagonal system,** like the preceding, frequently exhibits elongated prismatic forms, but the section of the crystals is a hexagon, instead of a square, and the termination is a six-sided pyramid. Quartz (Fig. 42), or rock crystal, is the most familiar mineral in this system. Calcite ($CaCO_3$), which is chemically identical with chalk, or marble, takes forms known as the scalenohedron (Fig. 43) and rhombohedron (Fig. 44), which are classified in a subdivision of this system. Indeed, recently it has become common to erect this into a separate system (the trigonal), in which both quartz and calcite are included.

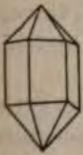

Fig. 42.

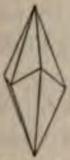

Fig. 43.

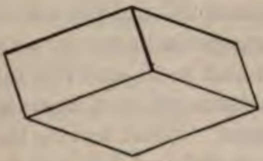

Fig. 44.

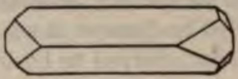

Fig. 45.

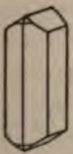

Fig. 46.

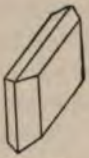

Fig. 47.

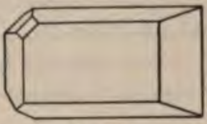

Fig. 48.

The **rhombic system** includes the natural forms of the topaz, and of sulphur (Fig. 7, p. 12), as well as that of potassium permanganate (Fig. 45), potassium nitrate (Fig. 46), and many other substances. These crystals exhibit a good deal of symmetry, but their section is always rhombic, and hence the name.

The **monosymmetric system** exhibits forms which have but one plane of symmetry. Gypsum (Fig. 47), which is hydrated calcium sulphate $CaSO_4,2H_2O$, and feldspar (Fig. 3, p. 2) are minerals possessing forms of this kind. Tartaric acid, rock candy (Fig. 48), potassium chlorate, and hydrated sodium carbonate (washing soda) belong to this system.

The **asymmetric system** includes forms which have no plane of symmetry whatever. Blue vitriol (Fig. 52, p. 95), $CuSO_4,5H_2O$, is one of the most familiar substances of this kind.

Exercises. — The text cannot be understood unless some problems involving the laws of gases are actually worked.

1. Reduce 189 c.c. of gas at 15° and 750 mm. to 0° and 760 mm.
2. Reduce 110 c.c. of gas at −5° and 741 mm. to 0° and 760 mm.
3. Convert 500 c.c. of gas at 25° and 700 mm. to 18° and 745 mm.
4. Reduce 250 c.c. of gas (standing over water) at 22° and 755 mm. to the dry condition and to 0° and 760 mm.
5. The density of a substance referred to air is 3.2. What is the density referred to hydrogen? What will be the volume occupied by 10 g. of the substance at 20° and 752 mm.?
6. Describe two ways of obtaining crystals of a substance.

CHAPTER VIII

WATER

WATER is as necessary to life as is oxygen. The human body is saturated with it and, to make up for evaporation, as well as to aid in digestion and other life processes, it is a necessary part of our food. The ocean covers three-fourths of the earth's surface, and the "dry" land is, fortunately, far from being really dry.

Physical Properties of Water. — A deep layer of water has a blue or greenish-blue color. At a pressure of 760 mm., water exists as a liquid between 0° and 100°. Below 0° it becomes solid, above 100° a gas. Of all chemical substances it is the one which we use most, so that its physical properties, discussed below, should be studied attentively. Then, too, what is said of water is in general true of all other liquids, from which it differs only in details.

The quantity of heat required to raise one gram of water one degree in temperature, at 15°, is called a **calorie**, the unit quantity of heat. The specific heat of any substance being the quantity of heat required to raise the temperature of one gram of the substance one degree, the specific heat of water is 1. The values for other substances are all smaller (*e.g.*, limestone 0.2). Thus the temperature of large masses of water, such as lakes and seas, changes more slowly, and within a smaller range, than that of the rocks and soil composing the land. The more constant temperature of the water tends to regulate that of the air, and hence the climate of an island is less variable from season to season than is that of a continent.

Ice. — The raising or lowering of the temperature of a gram of water through one degree involves the addition or removal of one calorie of heat. The conversion, however, of a gram of water at 0° to a gram of ice at 0° requires the removal of 79 calories. The mere melting of a gram of ice causes an absorption of heat to the same amount, called the **heat of fusion of ice.** At 0° a mixture of ice and water will remain in unchanged proportions indefinitely. Any cause which tends *permanently* to lower or raise the temperature by a fraction of a degree, however, will bring about the disappearance of the water or of the ice, respectively. This temperature is called the **melting-** or the **freezing-point.**

Water can be cooled below 0° (supercooled) without beginning to freeze, unless it is stirred, or "inoculated" by the addition of a piece of ice. Hence, the freezing-point is not defined as the point at which ice begins to form, for that point varies, and is always below 0°, but as the temperature of a *mixture* of ice and water.

Steam. — At atmospheric pressure, water passes into steam rapidly at 100°, but at lower temperatures, and even when frozen, it does the same thing more slowly. It changes into steam, however, only when the necessary supply of heat is forthcoming. One gram of water at 100°, in turning into a gram of steam at 100°, takes up 540 calories. This is called its **heat of vaporization.** Steam, in fact, contains much more internal energy than an equal weight of water at the same temperature, just as water, in turn, contains more energy than ice.

Steam is a colorless, invisible gas. The visible cloud of fog, seen when steam escapes into cold air, is composed of minute drops of water, formed by condensation, and visible because they have *surfaces* and reflect light.

The States of Matter: Transition Points. — Most substances are known in three different states of aggregation, solid (crystalline), liquid, and gaseous. There is no magic about the number, three, however. Thus, sulphur has a vapor state, two liquid states, and several solid forms. There are even five forms of ice, and most solids probably exist in several different states.

All transitions from one state to another take place at some definite temperature (when the pressure is fixed). Such temperatures, when referring to the change from the solid to the liquid, and from the liquid to the gaseous state are called the melting-point or freezing-point, and the boiling-point, respectively, or in general, are known as **transition points.**

Aqueous Tension and Vapor Pressure. — The quantity of the vapor present is defined by the gaseous pressure it exercises, the value being called the **vapor pressure** of water vapor (or of the vapor of any other volatile substance) in the location in question.

The most significant fact about vapor pressure is that, *when excess of the liquid is present*, the pressure of the vapor quickly reaches a definite maximum value for each temperature. In the absence of excess of the water, *less* than this maximum pressure may exist. *More* than the maximum pressure proper to a given temperature, if produced by compression, cannot be maintained, however, for a part of the vapor condenses to the liquid state. The magnitude of this maximum vapor pressure, at a given temperature, depends on the ability of the particular liquid to generate vapor. This maximum vapor pressure is held, therefore, to represent the **vapor tension of the liquid,** at the given temperature, and this is a specific property of the substance.

The vapor tension may be shown by allowing a few drops of water to ascend into a barometric vacuum (Fig. 49). The tube on the left shows the mercury when nothing presses on its surface. The tube on the right shows the result of admitting the water. The difference in the height of the two columns gives the value of the vapor pressure of the water vapor. With excess of water, the value is that of the vapor tension, called, in the case of water, the **aqueous tension.**

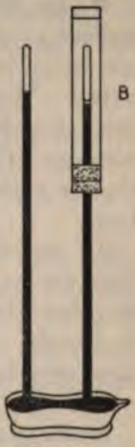

FIG. 49.

The jacket surrounding the tube on the right enables us, by adding ice or warm water, to maintain any temperature between 0° and 100°. When ice is used outside, and a piece of it is introduced into the vacuum, the vapor it gives off quickly reaches a pressure of 4.5 mm. The vapor pressure of the ice takes the place of 4.5 mm. of mercury in balancing the atmospheric pressure, and so the mercury column falls by this amount. Similarly, water at 10° causes a fall of 9.1 mm. and at 20° of 17.4 mm., so that these represent the mercury-height values of the aqueous tension at these temperatures. The *quantity* of water used makes no difference, so long as *a little more* is present than is required to fill the available space with vapor. With ether, instead of water, at 10°, the fall is 28.7 mm.

With water at higher temperatures the fall of the mercury column becomes much greater. At 50° it is 92 mm., at 70° it is 233.3 mm., at 90° it is 525.5 mm., and at 100° it is 760 mm., or one atmosphere. At 121° the aqueous tension is two atmospheres, at 180° it is ten atmospheres (see Appendix IV).

When water at a certain temperature has given the full amount of water vapor to the space above it that its aqueous tension permits, we say that the space is **saturated** with vapor. That **concentration** of vapor which constitutes saturation varies with the temperature of the water and depends, therefore, solely on the power of the water to give off vapor. It has nothing to do with the size of the space, and is even independent of other gases the space may already contain. Thus, if a little air is first placed above the dry mercury (Fig. 49), causing it to fall, the *additional* depression produced by adding water is the same as if the air had been absent (p. 72. See footnote to p. 11).

Water Vapor in the Air. — The space immediately above the surface of the ground, which is mainly occupied by atmospheric air, is, on an average, less than two-thirds saturated with water vapor. That is to say, such air, when enclosed in a vessel containing water, will take up about one-half more than it already contains. The vapor of water at 100° in an open vessel displaces the air entirely and, if the required heat is furnished, the liquid boils.

All our substances and apparatus have traces of water, derived from the atmosphere, **condensed on their surfaces.** This water is, in a sense, in an abnormal condition, for it does not evaporate even in dry air. It is observed to pass off in vapor, however, when we have occasion to heat the substance or apparatus.

Molecular Relations of Liquid and Vapor. — When the water was introduced above the barometric column, the vapor, or gaseous water, could have resulted only from the spontaneous motion of the molecules in the liquid. Some of the molecules, moving near the surface, went off into the space above the water and became gaseous. To be consistent, we must also conclude that the vapor above the water is not composed of the *same* set of molecules one minute as it was during the preceding minute. Their motions must cause many of them to plunge into the liquid, while others emerge and take their places. When the water is first introduced, there are no molecules of vapor in the space at all, so that emission from the water predominates. The pressure of the vapor increases as the concentration of the molecules of vapor becomes greater, hence the mercury column falls steadily. At the same time the number of gaseous molecules plunging into the water per second must increase in proportion to the degree to which they are crowded in the vapor. The rate at which molecules return to the water thus begins at zero, and increases steadily; the rate at which molecules leave the water maintains a constant value. Hence the rate at which vapor molecules enter the water must eventually equal that at which other water molecules leave the liquid. At this point, occasion for visible changes ceases and the mercury comes to rest. We are bound to think, however, of the exchange as still going on, since nothing has occurred to stop it. The condition is not one of rest but of rapid and equal exchange. Such, described in terms of molecules, is the state of affairs which is characteristic of a condition of **equilibrium.** The condition is dynamic, and not static.

Equilibrium. — This term is used so often in chemistry, and is used in so unfamiliar a sense, that the reader should consider attentively what it implies. Three things are characteristic of a state of equilibrium:

1. There are **always two opposing tendencies** which, when equilibrium is reached, balance each other. In the foregoing instance, one of these is the hail of molecules leaving the liquid, which is constant throughout the experiment. It represents the **vapor tension of the liquid.** The other is the hail of returning molecules, which, at first, increases steadily as the concentration of the vapor becomes greater. This is the **vapor pressure of the vapor.** These have the effect of opposing pressures and, when the latter becomes equal to the former, *equilibrium* is established. In all cases of equilibrium we shall symbolize the two opposing tendencies by *two* arrows, thus:

$$\text{Water (liq.)} \rightleftarrows \text{Water (vapor).}$$

2. Although their effects thus neutralize each other **at equilibrium, both tendencies are still in full operation.** In the case in point, the opposing hails of molecules are still at work, but neither can effect any visible change in the system. Equilibrium is a state, not of rest, but of balanced activities.

3 (and this is the chief mark of equilibrium). **A slight change in the conditions produces,** never a great or sharp change, but always, and instantly, **a corresponding small change in the state of the system.** The change in the conditions accomplishes this by **favoring or disfavoring one of the two opposing tendencies.** Thus, for example, when the *temperature* of a liquid *is raised*, the kinetic energy of its molecules is increased, the rate at which they leave its surface becomes greater, the vapor tension increases and, hence, a greater concentration of vapor can be maintained. The system, therefore, quickly reaches a new state of equilibrium in which a higher vapor pressure exists. A heap of matter on a table is not in equilibrium, because addition of more material produces no response until, when a very great quantity is added, the table breaks. But a body on the scales is in equilibrium, for the addition of the smallest particle produces a corresponding inclination of the beam.

In the preceding illustration, the evaporating tendency was *favored* by a rise in temperature. As an example of a change in conditions *disfavoring* one tendency, take the case where the liquid is placed in an *open*, shallow vessel. Here the condensing tendency is markedly discouraged, for there is practically no return of the emitted molecules. Hence complete evaporation takes place. Elevation of the temperature hastens the process. A draft insures the total prevention of all returns, and has therefore the same effect. The two methods of assisting the displacement of an equilibrium, and particularly the second, in which the opposed process is weakened and the forward process triumphs solely on this account, should be noted carefully. They are applied with surprising effectiveness in the explanation of chemical phenomena (see Chaps. XIV and XVIII).

Water as a Solvent. — One of those physical properties of water which are most used in chemical work is its tendency to dissolve many substances. This subject is so important and extensive that we shall presently devote a complete chapter to some of its simpler and more familiar aspects.

Natural Waters. — The foreign material in natural waters is divided into **dissolved** matter and **suspended** matter. Rain-water, collected after most of the dust has been carried down, is *the purest* natural water. It contains, however, nitrogen, oxygen, and carbon dioxide dissolved from the air. Sea-water holds about 3.6 per cent of dissolved material. River and, especially, well waters dissolve various substances during their progress over or under the surface of the ground. They often contain calcium sulphate, calcium bicarbonate, and compounds of magnesium, and are then described as **hard.** Sometimes they contain compounds of iron, and sometimes they are effervescent and give off carbon dioxide. These are called mineral waters.

Many river waters contain large amounts of clay and organic matter (often due to admixture of sewage) suspended in them. It is not the organic matter which is deleterious, but the bacteria of putrefaction and disease which are present also, and are usually for the most part attached to the particles of suspended matter. Cholera and typhoid fever are often spread by the drinking of water into which sewage, infected by other patients suffering from these diseases, has been allowed to enter. Clay can be seen, and renders the water turbid, but organic matter and bacteria may be present in water which looks perfectly clear.

Purification from Suspended Matter. — The suspended impurities may be removed by **filtration.** On a large scale, beds of gravel are employed, but this treatment will not remove all bacteria. In many cases small amounts of alum, or alum and lime, or ferrous sulphate (copperas) and lime, are added. These produce slimy precipitates which assist in the elimination of fine, suspended inorganic and organic matter, including practically all the bacteria. This is called the **coagulation treatment** (*q.v*). The whole suspended matter is then allowed to settle, which it does very quickly, in large reservoirs. The remaining organisms may be destroyed by adding a little bleaching powder (*q.v.*), before the water is distributed. Ozone and ultra-violet light are used for the same purpose.

In the household, the **Pasteur filter** is the most compact and efficient appliance. The water enters at the top (Fig. 50), and is forced inwards by its own pressure through the pores of a cylinder of unglazed porcelain. The cylinder must be taken out, and its exterior cleaned daily with a brush, to remove the mud and organisms which collect on its outer surface. If this is not done, the organisms multiply and soon the filter pollutes the water instead of purifying it.

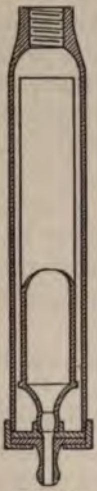
FIG. 50.

Most organisms can be killed by **boiling** the unfiltered water for 10 or 15 minutes, although a second boiling is needed in the case of some.

Purification from Dissolved Matter. — Filtration does not remove dissolved matter, and therefore does not soften hard water (*q.v.*).

Pure water for chemical purposes is prepared by distillation and, in fact, liquids other than water are usually purified by the same process (Fig. 51). The steam is condensed by cold water circulating in the jacket, and contains only gases dissolved from the air. Dissolved solids remain in the flask. Distilled water quickly dissolves traces of glass or porcelain, so that the purest water is obtained by using quartz or platinum for the condenser tube and receiving vessel. Tin is the best of the less expensive materials.

Chemical Properties of Water. — Water is so very frequently used in chemical experiments in which it is a mere mechanical adjunct, that the beginner has difficulty in distinguishing the cases in which it has itself taken part in the chemical interaction. The four kinds of chemical activity which it shows should therefore receive careful notice:

1. Water is a relatively stable substance.
2. It combines with many oxides, forming bases or acids.
3. It combines with many substances, chiefly salts, forming hydrates.
4. It interacts with some substances in a way described as hydrolysis. This property will not be discussed until a characteristic case is encountered.

Water a Stable Compound: Dissociation. — In the case of a *compound*, the first chemical property to be given is always, whether the substance is relatively **stable** or **unstable**. Usually the specification is in terms of the temperature required to produce noticeable decomposition. Thus, potassium chlorate gives off oxygen at a low red heat. Now, water vapor, when heated, is progressively decomposed into hydrogen and oxygen, yet at 2000° the decomposition reaches only 1.8 per cent, and reunion occurs as the temperature is lowered. The two arrows in the equation indicate that the action may proceed in either direction — is **reversible**:

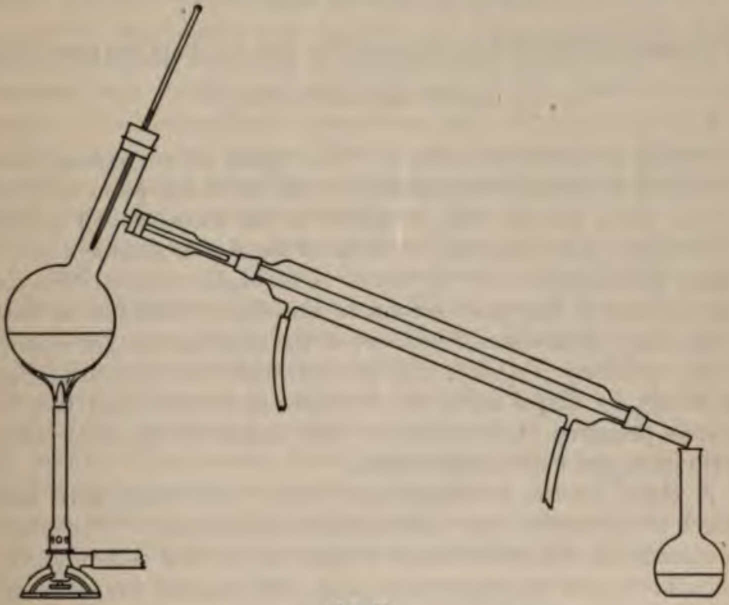

FIG. 51.

$$H_2O \rightleftarrows 2H + O.$$

A decomposition which thus proceeds at higher temperatures, while at lower temperatures combination of the constituents can take place, is called a **dissociation**. The decomposition of potassium chlorate (p. 27) is not a dissociation because it is not reversible; oxygen gas will not under any known circumstances unite with potassium chloride.

Union of Water with Oxides. — 1. Sodium oxide (Na_2O) unites violently with water to form sodium hydroxide:

$$Na_2O + H_2O \rightarrow 2NaOH.$$

The slaking of quicklime is a more familiar action of the same kind:

$$CaO + H_2O \rightarrow Ca(OH)_2.$$

No other products are formed. The clouds of condensing steam produced in the second instance are due to evaporation of a part of the water by the heat produced in the formation of calcium hydroxide. The aqueous solutions of these two products have a soapy feeling, and turn red litmus (a vegetable extract) blue, and the substances therefore belong to the class of alkalies or **bases.** Very many hydroxides, which are of the same nature, for example ferric hydroxide $Fe(OH)_3$ and tin hydroxide $Sn(OH)_2$, are formed so slowly by direct union of the oxide and water that they are always prepared in other ways. The oxides which, with water, form bases are called **basic oxides.**

2. Some oxides, although they unite with water, give **acids,** which are products of an entirely different character. Phosphorus pentoxide (p. 32) and sulphur dioxide are of this class and yield phosphoric acid and sulphurous acid. Such oxides are commonly called the **anhydrides** (Gk., *without water*) of their respective acids. They are called also **acidic oxides:**

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4.$$
$$SO_2 + H_2O \rightarrow H_2SO_3.$$

The acids are sour in taste and turn blue litmus red.

These two classes of final products are so different that we make the distinction the basis for classification of the elements present in the original oxides. The elements, like sodium and iron, whose oxides give bases, are called **metallic elements;** those, like phosphorus, whose oxides give acids, are called **non-metallic elements.** The distinguishing words are selected because the division corresponds, in a general way at least, with the separation into two sets to which merely physical examination of the elementary substances would lead.

Hydrates. — Many substances when dissolved in water and recovered by spontaneous evaporation of the solvent enter into combination with the liquid. The products, which are solids, are called **hydrates.** That they are regular chemical compounds is shown by the following two facts: (1) These compounds show definite chemical composition expressible by formulæ in terms of chemical unit weights (atomic weights) of the constituent elements. The proportions in solutions and other physical aggregations, except by chance, cannot be expressed by means of formulæ. (2) A hydrate has physical properties entirely different from those of the water (or ice) and the other substance used in preparing it. It is a typical compound, formed by the first variety of chemical change (p. 7). Thus, cupric sulphate, often called anhydrous cupric sulphate to distinguish it from the compound with water, is a white substance crystallizing in shining, colorless, needle-like prisms. The pentahydrate (blue-stone or blue vitriol) which crystallizes from the aqueous solution, is blue in color, and forms larger but much less symmetrical (asymmetric or triclinic) crystals (Fig. 52):

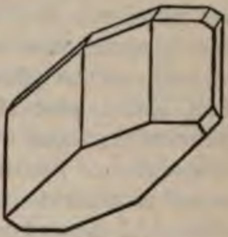

FIG. 52.

$$CuSO_4 + 5H_2O \rightleftarrows CuSO_4,5H_2O.$$

The **chemical properties** show hydrates to be relatively unstable. When heated, the hydrates, as a rule, lose none of the constituents of the original compound, but only the water, in the form of vapor. When melted, or when dissolved in water, the hydrates are dissociated (p. 93) into water and the original substance. The aqueous solutions made from the anhydrous substances and from the hydrates have identical physical and chemical properties. Hence the cheaper of the two forms is generally purchased, and many of the chemicals used in the laboratory are in the form of hydrates.

In consequence of the ease with which hydrates give up water we write their formulæ (*e.g.*, $CuSO_4,5H_2O$) so that the water and original substance are separate. A formula thus modified, so as to show some favorite mode of behavior of the substance, is called a **reaction formula.** The formula $H_{10}CuSO_9$, which would show the same proportions by weight, is never employed, because its use would disguise the relation of the substance to cupric sulphate.

The Dissociation of Hydrates. Efflorescence. — The less stable hydrates dissociate very readily. Thus the decahydrate of sodium sulphate, $Na_2SO_4,10H_2O$ (Glauber's salt), loses all the water it contains (**effloresces**) when simply kept in an open vessel. When kept in a *closed* bottle, a very little of it loses water, and then the decomposition ceases. The cause of this we discover when a crystal of the hydrate is placed above mercury, like the ice or water in Fig. 49 (p. 87). *It shows an aqueous tension* which we can measure. At 9° the value of this is 5.5 mm. As its temperature is raised, the tension increases. When the temperature is lowered, on the other hand, the tension diminishes, the mercury rises, and a part of the water enters into combination again. Different hydrates show different aqueous tensions at the same temperature. For example, at 30°, that of water itself is 31.5 mm., strontium chloride $SrCl_2,6H_2O$, 11.5 mm.; cupric sulphate $CuSO_4,5H_2O$, 12.5 mm.; barium chloride $BaCl_2,2H_2O$, 4 mm.

In view of these facts, we perceive that loss of water by efflorescence is like evaporation, excepting that it is a chemical decomposition and not a physical process. Those hydrates which, like Glauber's salt and washing soda $Na_2CO_3,10H_2O$, have a vapor tension approaching that of water itself, lose their water at ordinary temperatures at a rapid pace. Now, atmospheric air is usually less than two-thirds saturated with water vapor, and the partial pressure (p. 72) of this vapor *opposes the dissociation* and tends to prevent the liberation of the water. Thus at 9°, the vapor tension of water being 8.6 mm., the average vapor pressure of water in the atmosphere will be about 5 mm. Any hydrate with a greater aqueous tension than 5 mm. at 9°, such as Glauber's salt, will therefore decompose spontaneously in an open vessel. But those with a lower vapor tension, such as the pentahydrate of cupric sulphate with a tension of 2 mm. at 9°, will not do so. Granular calcium chloride $CaCl_2,2H_2O$ is used in drying gases because it has an exceedingly low tension of water vapor, and combines with water vapor to form $CaCl_2,6H_2O$.

The water of hydration is known colloquially in chemistry as **water of crystallization.** The term was introduced when it was first observed that a hydrate, in decomposing, crumbles and loses its original crystalline form. But the phrase is misleading. Sulphur, potassium chlorate, and thousands of other substances are crystalline, yet do not contain the elements of water. All pure chemical substances, in solid form, when in stable physical condition, are crystalline. Amorphous (*i.e.*, non-crystalline) substances, like wax and glass, are supercooled liquids.

How Formulæ and Equations are Obtained. — In the last few pages several formulæ (*e.g.*, of hydrates) and several new equations have been given. How do we know what to set down in making an equation? We cannot learn this by simply writing formulæ on a piece of paper. In each case, experiments must be made in the laboratory. For example, how do we know that the common hydrate of cupric sulphate has the formula $CuSO_4,5H_2O$, and not $CuSO_4,H_2O$? We must make a quantitative experiment. We weigh a porcelain dish or crucible, first empty, and then with a little of the hydrate. Suppose the difference in weight to be 2.05 g. (= weight of hydrate). We then heat the dish and contents, until the water is driven out, and weigh again. The difference is now only 1.31 g. (wt. of anhydrous cupric sulphate). The water, therefore, weighed $2.05 - 1.31 = 0.74$ g. Assuming that we know the formulæ (compositions) of cupric sulphate and of water, we obtain their formula-weights: $CuSO_4 = 63.57 + 32.06 + 4 \times 16 = 159.63$; and $H_2O = 2 \times 1.008 + 16 = 18.016$. The formula must be $CuSO_4,xH_2O$. Also

$$159.63 : x \times 18.016 :: 1.31 : 0.74.$$

Solving for x, we have $x \times 18.016 \times 1.31 = 159.63 \times 0.74$, or $x = 159.63 \times 0.74/18.016 \times 1.31 = 5.00$. The formula is therefore $CuSO_4,5H_2O$, and the equation for the decomposition:

$$CuSO_4,5H_2O \rightarrow CuSO_4 + 5H_2O.$$

To make an equation, we must note what substances are taken, and recognize by their properties all the substances produced. If all the substances are well known, and we can find their formulæ in a book, we can make the equation at once. If we cannot find the formulæ, we make measurements to determine the proportions by weight, calculate the formulæ, and then make the equation.

Composition of Water. — The proportion of hydrogen to oxygen, in water, **by weight,** is 2 : 15.879, or 2.016 : 16. The proportion **by volume** is 2.0027 volumes of hydrogen to 1 volume of oxygen. That the proportion by volume is very close to 2 : 1 may easily be shown by mixing hydrogen and oxygen in this proportion, in a strong tube, and exploding the mixture by means of a spark from an induction coil. The resulting steam condenses and the whole gas vanishes. If different proportions are used, the excess of one of the gases remains uncombined.

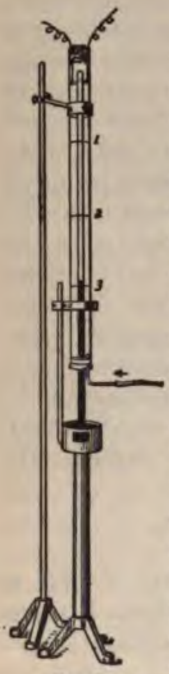

FIG. 53.

Gay-Lussac's Law of Combining Volumes. — The almost mathematical exactness with which small integers express this proportion is not a mere coincidence. **Whenever gases unite, or gaseous products are formed, the proportions by volume** (measured at the same temperature and pressure) **of all the gaseous bodies concerned can be represented very accurately by ratios of small integers.** This is called **Gay-Lussac's law of combining volumes** (1808). Thus, when the above experiment is carried out at 100°, in order that the product, water, may be gaseous also, it is found that the three volumes of the constituents give almost exactly two volumes of steam. For example, 15 c.c. of hydrogen and 7.5 c.c. of oxygen give 15 c.c. of steam. Of course the hydrogen, oxygen, and steam must be measured at the same pressure, and the temperature must remain constant (100°) during the experiment. Proper manipulation secures the former, and a jacket filled with steam (Fig. 53) the latter condition. Strips of paper, 1, 2, and 3, are pasted on the jacket in such a way that equal lengths of the eudiometer, in this case a straight one, are laid off. The three divisions being filled with a mixture of hydrogen and oxygen in the proper proportions, the gas, after the explosion, shrinks so as to occupy, at the same pressure, only two of them.

Exercises. — 1. Name some familiar transitions (p. 86) from one physical state to another.

2. What evidence is there in the common behavior of ether and chloroform to show that these liquids have high vapor tensions?

3. If the pressure of the steam in a boiler is ten atmospheres, at what temperature is the water boiling (p. 88)?

4. How many grams of water could be heated from 20° to 100° by the heat required to melt 1 kg. of ice at 0°?

5. What do you infer from the fact that alum and washing soda lose their water of hydration when left in open vessels, while gypsum does not?

6. Which fact shows most conclusively that hydrates are true chemical compounds?

7. Gypsum is a hydrate of calcium sulphate ($CaSO_4$). If 6 g. of gypsum, when heated, lose 1.256 g. of water, what is the formula of the hydrate?

8. In what ways does a hydrate differ from, (*a*) a solution, (*b*) an hydroxide?

9. Should you expect to find any difference, in respect to chemical activity, between the three forms of water? Have we had any experimental confirmation, or the reverse, of this conclusion (p. 51)?

10. Name some crystalline substances which are not used, or do not occur in the form of hydrates.

11. Define the purposes for which evaporation and distillation are used.

CHAPTER IX

MOLECULAR WEIGHTS AND ATOMIC WEIGHTS

GAY-LUSSAC's law (p. 98) shows that, when substances are measured in the *gaseous* condition, and *by volume* (not by weight), the proportions in which they combine can be represented by small whole numbers, such as 2 : 1, or 1 : 1, or 2 : 3. The numbers are much simpler than when proportions *by weight* are employed. Thus, lead and oxygen combined in the proportions 100 : 7.72 by weight. It would seem, therefore, that the shortest route to simple methods for expressing combining proportions must lie through a study of volumes of gases and vapors.

MOLECULAR WEIGHTS

The Chemical Unit of Volume for Gases: 22.4 Liters.— The first thing we require is a suitable unit volume. In making a choice, we have to keep in mind the fact that many substances cannot easily be converted into vapor, and that therefore measurement of gaseous volumes cannot entirely displace the measurement of weights. The measurement of gaseous volumes is only to furnish the key to the system. Hence, in choosing our unit volume of gas, we must choose one which bears a simple relation to our units of weight. Now, the **unit of volume** chosen is **that of 32 grams of oxygen,** which, **at 0° and 760 mm. pressure,** is **22.4 liters.**

At this stage, it may appear that this is an unduly large unit — that 16 grams of oxygen, occupying 11.2 liters, might have sufficed. As we proceed, however, we shall find that a smaller unit than 22.4 liters leads to a number less than unity for the atomic weight of hydrogen. There is no theoretical or chemical objection to a unit involving an atomic weight for hydrogen that is less than 1, but chemists are unanimous in preferring to have an arithmetical unit in the scale, simply as a matter of convenience. So, reasoning back from this decision, they have found it necessary — we shall perceive the reason presently — to choose **22.4 liters** in the **gaseous condition** as the **unit quantity of a substance.**

We shall understand what follows much more readily if we have before us, in our minds at least or, better still, in the form of a wooden box, a representation of this unit volume (Fig. 54). A cube 11.1 inches in height holds 22.4 liters. It is to be understood that under conditions other than 0° and 760 mm., this unit volume changes in accordance with the laws of gases. In this way, it always contains the same quantity of a given kind of gas. In what follows, the standard conditions are assumed, unless other conditions are specifically mentioned.

FIG. 54.

Weights Occupying the Unit Volume — 22.4 Liters. — In order that we may keep in touch with the weights, the following table gives the weights of equal volumes of several gases and vapors. The first column contains the weights of 1 liter. The one-thousandth part of each of these weights is the **density** * (p. 73) of the gas (weight of 1 c.c.). The experimental method of measuring the weight of 1 liter of a gas has already been described (p. 73). In the second column are the weights of 22.4 liters, obtained by multiplying the values in the first column by 22.4. It will be observed that the weights of equal volumes of the gases cover a wide range of values from 2 for hydrogen (col. 3) to 271.5 for mercuric chloride.

Gases or Vapors.	Weight* of One Liter, 0° and 760 mm.	Weight of 22.4 Liters (Molecular Weight).
Hydrogen	0.090	2.016
Oxygen	1.429	**32.00**
Chlorine	3.166	70.92
Hydrogen chloride	1.628	36.468
Carbon dioxide	1.965	44.00
Water	0.8045	18.016
Mercury	8.932	200.6
Mercuric chloride	12.097	271.52
Air	1.293	28.955

* These weights are corrected for the two deviations from the laws of gases (pp. 78–79).

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* Sometimes density is expressed on the basis air = 1. One liter of air weighs 1.293 g. Hence, if one liter of a gas weighs 3.6 g., its density, air = 1, is found by the proportion: 1.293 : 1 :: 3.6 : x.

The values for the vapors of water (b.-p. 100°), mercury (b.-p. 357°), and mercuric chloride (b.-p. 300°) are measured at high temperatures and reduced by rule (pp. 71–72) to 0° and 760 mm.

Molecular Weights. — In this discussion of volumes and of weights, we must not overlook the interpretation of our results in terms of molecules. The masses of gas we handle are aggregates of molecules, and the molecules are physically the real units of matter.

Now, according to Avogadro's law, equal volumes of gases (at the same *t.* and *p.*) contain equal numbers of molecules. The weights in each column of the table are therefore weights of equal numbers of molecules. The chemical units in the last column show, therefore, **the relative weights of the individual molecules of the substances named.** On this account they are called the **molecular weights** of the respective substances.

Since the 22.4-liter volume holds 32 *grams* of oxygen and 2.016 *grams* of hydrogen — the gram being used throughout — this volume is called the **gram-molecular volume** (G.M.V.) and the weights just mentioned are the **gram-molecular weights.** Frequently, these ponderous terms are shortened to **molar volume** and **molar weight,** and the latter even to **mole.** Thus, a mole of chlorine is 70.92 g. of the simple substance and a *mole* of hydrogen chloride is 36.468 g. of the compound.*

Measurement of Molar Weights (Moles). — We may now state, in brief, the **method of finding the molar (gram-molecular) weight of a substance thus: Weigh a known volume of the substance,**

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* A common question is: Do not molecules of different substances differ in size, and will not the numbers required to fill the G.M.V. therefore be different? The answer is that the molecules are all so small compared with the spaces between them (at 760 mm.) that the distances from surface to surface are practically the same as from center to center. A G.M.V. of oxygen, when liquefied, gives less than 32 c.c. of liquid oxygen, or less than 1/700 of the volume as gas. It is only when gases are so severely compressed that the nearness of the molecules to one another approaches that found in the liquid condition that the effects of the bulk of the molecules become conspicuous, and a difference in the behavior of different gases is noticeable. But in the work discussed in this chapter, pressures over one atmosphere are intentionally avoided.

at any temperature and pressure at which it is gaseous, reduce this volume by rule to 0° and 760 mm., and calculate by proportion the weight of 22.4 liters (see Exercises 1, 2, 3, 5).

That quantity of each gaseous substance which at 0° and 760 mm. would fill the G.M.V. cube is the unit quantity of the substance for all theoretical purposes in chemistry. It represents the relative weight of the molecules of the substance. We shall employ it presently for the purpose of determining the *relative weights of atoms*, or atomic weights.

The Number of Molecules in a Mole. — The molecular weight or mole of a substance is not the weight of a single molecule. It is only the *relative* weight of the molecule of the substance. It is, however, the weight in grams of a fixed number of molecules, for 22.4 liters (or any other volume) contains equal numbers of molecules of different gases. The actual number has been determined. Thus Jean Perrin found values by several experimental methods which ranged between 5.9×10^{23} (that is, 59 followed by 22 ciphers) and 6.9×10^{23}. Rutherford, using an entirely different plan, obtained 5.7×10^{23} for the gas helium. The value which is accepted as most accurate was that obtained by R. A. Millikan of the University of Chicago, by the use of a still different method, namely, 6.07×10^{23} (or 6070_{21}).

Atomic Weights

Chemical Unit Quantities of Elements. — We are now approaching the question of units, in which to express combining proportions, from a different view point from that employed in the earlier chapters. We were then assigning numbers for the quantities of the constituent elements of a compound (such as iron : oxygen :: 111.68 : 48, p. 9) without any consideration of the magnitude of the *total weight* of the constituents. At that time, we had no reason before us to indicate that this total might require consideration. We now *start* by determining and assigning the total weight of the compound, and it is our next task to consider the subdivision of this total amongst the constituents. Evidently, if the unit quantity of the compound has been properly chosen, it must be subdivisible into one or more unit quantities, of suitable dimensions, of each element in the compound. Let us now set down, and examine the results of such a subdivision in the case of several compounds. To be more precise, we take 22.4 liters of *every* substance — one cubeful in the gaseous condition — as the total quantity. We make an analysis of a sample of the substance, in case it is a compound, to ascertain the proportions in which the elements are present in it. We then divide the weight of 22.4 liters of the compound between the different elements in the proportion shown by the analysis.

For example, the cube holds 36.468 g. of hydrogen chloride gas. This amount, when decomposed, yields 1.008 g.* of hydrogen and 35.46 g. of chlorine.

Another example: Suppose the substance is a liquid, like phosphorus oxychloride. We determine the weight of a measured volume of its *vapor,* at a properly chosen temperature and pressure, and the result gives us, by calculation, the weight of 22.4 liters, the molecular weight, *viz.,* 153.38. That is, 153.38 g. of the substance would fill the cube, if it could be kept as vapor at 0° and 760 mm. The analysis shows that *this amount* of the substance contains 31 g. of the element phosphorus, 16 g. of the element oxygen, and 106.38 g. of the element chlorine.

In the following **table** a few **sample results of the process just outlined** are given. The first column contains the molar weight, *i.e.,* the weight of the substance which occupies the G.M.V. cube. In the other columns are entered the weights of the various elements which together make up the total molar weight. To simplify the numbers, the values used are hydrogen 1, phosphorus 31, mercury 200, instead of 1.008, 31.04, and 200.6, respectively.

Atomic Weights. — To contain similar data for all the volatile compounds of every known element, a huge table, of which this might be a small corner, would be required. With such a table at hand the atomic weight of each element could promptly be picked out. Thus, in the carbon column it would be found that all the weights of carbon were either 12 or integral multiples of 12, and

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* It will be observed that if the unit for molecular weights had been *less* than the number of molecules in 22.4 liters of oxygen, then an equal number of molecules of hydrogen chloride would have contained less than 1.008 g. of hydrogen, and the atomic weight of this element would then have been less than unity.

Substance.	Molar Weight.	Weights of Constituents in Molar Weight.						
		Hydrogen.	Chlorine.	Oxygen.	Phosphorus.	Carbon.	Mercury.	Molecular Formula.
Hydrogen chloride	36.46	1	35.46	....	....	....	....	HCl
Chlorine dioxide	67.46	....	35.46	32	....	....	....	ClO_2
Phosphorus trichloride	137.38	....	106.38	....	31	....	....	PCl_3
Phosphorus oxychloride	153.38	....	106.38	16	31	....	....	$POCl_3$
Phosphorus pentoxide	284	....	....	160	124	....	....	P_4O_{10}
Phosphine	34	3	....	....	31	....	....	PH_3
Water	18	2	....	16	....	....	....	H_2O
Methane	16	4	....	....	....	12	....	CH_4
Acetylene	26	2	....	....	....	24	....	C_2H_2
Ethylene	28	4	....	....	....	24	....	C_2H_4
Formaldehyde	30	2	....	16	....	12	....	CH_2O
Acetic acid	60	4	....	32	....	24	....	$C_2H_4O_2$
Mercurous chloride	235.46	....	35.46	....	....	....	200	$HgCl$
Mercuric chloride	270.92	....	70.92	....	....	....	200	$HgCl_2$

this is therefore the most convenient unit weight (and therefore the atomic weight) of carbon. Similarly, the atomic weight of oxygen is 16,* of phosphorus 31, of mercury 200 (see Exercise 4).

The fact that *all* the numbers in any one column turn out to be even multiples of a single number need not seem mysterious. The molecule of every compound containing chlorine must contain one, two, three, or some other *whole* number of chlorine atoms, for chlorine atoms, like other atoms, do not furnish fractions of atoms in any cases of combination. Now, the weight of chlorine in 6070_{21} atoms, assuming one atom of chlorine to each molecule in 22.4 liters of some gas containing chlorine, must be 35.46 g. Hence, if the weight of chlorine in 22.4 liters (6070_{21} molecules) of the compound differs from 35.46 g., it can do so only because there are two atoms of chlorine per molecule, giving 2 × 35.46 g., or three atoms giving 3 × 35.46 g. of chlorine, and so forth. Thus the quantities of chlorine in the G.M.V. of *all* compounds of chlorine must be a multiple of 35.46 by unity or some other integer.

When the atomic weights have finally been selected, we can go through the table and change all the numbers into multiples of the chosen atomic weights. Thus, for 70.92 we write 2 × 35.46, and for 106.38 we write 3 × 35.46, and so forth. The reader should prepare such a modification of the table. With this new form of the table before us, we can, finally, replace the atomic weights by the symbols which stand for them, writing, for 35.46, Cl, for 2 × 35.46, Cl_2, and so forth. The results of doing this in each line, *i.e.*, for each substance, are collected at the ends of the lines in the last column of the table. The reader should himself repeat the substitutions of the symbols, and so verify the formulæ given. These formulæ, since they are based on the molecular weights, in such a way that when the numerical values are substituted for the symbols the total restores to us the molecular weight, are called **molecular formulæ.**

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* The difference between the unit quantity of oxygen in compounds (namely 16) and the unit quantity of free oxygen (32) will be discussed presently.

As a **definition,** the **atomic weight of an element** may be stated to be: **The smallest of the weights of the element found in the molecular weights of all its volatile compounds,** so far as these have been examined.

It is hardly necessary to add that the atomic weights, found as described above, are equally serviceable in expressing the compositions of compounds which are *not* volatile. The atoms in non-volatile compounds are identical in properties with the atoms of the same elements in volatile compounds. If an element gives no volatile compounds, other methods of fixing its atomic weight are available (see Dulong and Petit's law, p. 108).

Although in this section, as well as elsewhere, we have emphasized the fact that atoms are not divided into parts, this must not be taken to mean that atoms are incapable of being broken up. It means only that in ordinary chemical changes, the atoms combine and separate as wholes. Indeed, we now know that the atom of radium (*q.v.*) gives off atoms of helium, and leaves an atom of lead, and that the atoms of one or two other elements *disintegrate* in a similar way. Some day means of breaking up any or all kinds of atoms may be discovered.

Many chemists have contributed to the determination and revision of the atomic weights. The Swedish chemist, Berzelius, devoted many years to the accurate measurement of combining proportions. Stas, a Belgian (1860–1870), made a number of determinations with great exactness. Morley's (1895) value for combining proportions of hydrogen and oxygen alone represented several years of work. T. W. Richards of Harvard University has recently carried many of the values to a higher degree of accuracy.

Why 22.4 Liters was Chosen as the Unit Volume. — We can now see why the volume occupied by 32 g. of oxygen, namely, 22.4 liters, was taken as the standard for the scale of molecular quantities. This gave us, for example, 36.468 g. as the weight of 22.4 l. of hydrogen chloride, which in turn contains 1.008 g. of hydrogen. A smaller weight of oxygen, with correspondingly smaller standard volume, would have held an amount of hydrogen chloride (and of other compounds containing one atom of hydrogen per molecule) which would have been *less than* 1 gram. The choice was made to secure something close to an arithmetical unit in the scale.

Advantages of Atomic Weights. — Although the method of selecting atomic weights involves rather complex reasoning, these weights repay the trouble, because they represent the relative weights of the atoms themselves. They are thus much more valuable in helping us to understand chemical behavior and in enabling us to classify the phenomena of chemistry than would be any other units of weight we might have chosen. The following are some of the advantages they offer:

1. The atomic weight of an element has but one value, and this value is definitely determinable. The advantages of using Avogadro's principle (1811), and taking a unit volume of gas as the basis of chemical units, were not perceived by chemists until Cannizzaro, in 1858, succeeded in setting them forth in a convincing manner. Previous to that time, different chemists used different unit weights for the same element, and therefore assigned different formulæ to the same compound, and much confusion existed. After 1858 chemists united upon the present values for atomic weights.

2. The atomic weight of an element has a valence (p. 61), while equivalents are equi-valent. While valence is a helpful conception in all branches of chemistry, organic chemistry is especially indebted to the conception of the quadrivalence of carbon for much of its development and most of its organization. The full illustration of this point is beyond the limits of the present book.

3. The periodic system (*q.v.*), the basis of a plan for classifying the properties of all chemical substances, is founded upon the atomic weights.

4. Dulong and Petit's law is based upon atomic weights. This law furnishes also an alternative means of determining atomic weights that has frequently rendered valuable service, and on this account forms the subject of the next section.

Dulong and Petit's Law, an Alternative Means of Determining Atomic Weights. — It was first pointed out (1818) by Dulong and Petit, of the École Polytechnique in Paris, that when the **atomic weights of the elements were multiplied by the specific heats of the simple substances in the solid condition, the products were approximately the same in all cases.** In other words, the specific heats are inversely proportional to the magnitudes of the atomic weights. The table, in which round numbers have been used for the atomic weights, shows that the product lies usually between 6 and 7, averaging about 6.4:

Element.	Atomic Wt.	Sp. Ht.	Product.	Element.	Atomic Wt.	Sp. Ht.	Product.
Lithium	7	0.94	6.6	Iron	56	0.112	6.3
Sodium	23	0.29	6.7	Zinc	65.4	0.093	6.1
Magnesium	24.3	0.245	6.0	Bromine (Solid)	80	0.084	6.7
Silicon	28.3	0.16	4.5	Gold	197	0.032	6.3
Phosphorus (Yellow)	31	0.19	5.9	Mercury (Solid)	200	0.0335	6.7
Calcium	40	0.170	6.8	Uranium	238.5	0.0276	6.6

Another way of expressing this law will give it greater chemical significance. The specific heats are the amounts of heat required to raise one gram, that is one *physical* unit, of each element through one degree. When we multiply this by the atomic weight, we obtain the amount of heat required to raise one gram-atomic weight of the element, that is, one chemical unit, through one degree. The values of this product are approximately equal. Since there are equal numbers of atoms in one gram-atomic weight of each element, it follows that: **Equal amounts of heat raise equal numbers of atoms of all elements in the solid form through equal intervals of temperature.**

It will be seen at once that, although the law of Dulong and Petit is purely empirical, it may nevertheless be **used for fixing the atomic weight of an element of which no volatile compounds are known.** We can always measure that weight of such an element which combines with *one atomic weight of another element.* Since the elements concerned must combine atom for atom, or in some simple ratio such as 1 : 2 or 2 : 3, it follows that the weight found is either the atomic weight or some multiple or submultiple of it by a whole number. When, therefore, we multiply this weight by the specific heat, we discover at once whether the product is 6.4 or some simple fraction or multiple of this number. For example, suppose the atomic weight of calcium to be unknown. We find by analysis that calcium chloride contains 20 parts of calcium combined with 35.46 parts (the atomic weight) of chlorine. Now the specific heat of solid, metallic calcium is 0.170. This number multiplied by 20 gives as the product 3.4. Evidently, therefore, the atomic weight is not 20, but 40, for the product, 6.8, then agrees fairly well with the average for other elements.

MOLECULAR FORMULÆ

Molecular Formulæ of Compounds. — If the molar formulæ in the table (p. 105) be examined it will be observed that several are not in their simplest terms. Thus, the formula of acetylene is C_2H_2. The formula CH would represent the composition of the substance equally well, for 12 : 1 is the same as 24 : 2. But the formula CH gives a total of only 13, while C_2H_2 shows the total weight of the molecule to be 26 and records for us therefore *the weight of the G.M.V.*, as well as the composition of the substance. We shall find this additional property, peculiar to the molecular formula, to be a feature of the greatest practical value. Some of the practical uses of this improvement in our formulæ will be illustrated in this chapter, and there is an example of one of them in the table itself. Thus, the molecular formula of acetic acid is $C_2H_4O_2$, and not the simpler, identical proportion CH_2O. The latter is the molecular formula of a totally different substance, formaldehyde, now much used as a disinfectant. The vapor of this substance has only half the density of acetic acid vapor, and this fact, recorded in the formula, helps to remind us that the substances are different. Still another substance of the same composition is grape sugar (dextrose), $C_6H_{12}O_6$. In addition to this and other practical advantages, molecular formulæ satisfy also the claim of logical consistency. If the symbols represent the atomic weights, the formulæ should be constructed so as to represent the molecular weights.

Molecular formulæ like C_2H_2 and $C_2H_4O_2$ are easily interpreted in terms of the atomic hypothesis. C represents one atom of carbon and H one atom of hydrogen. But there is no reason why a molecule of acetylene should not contain two atoms of each kind. Similarly, the molecule of formaldehyde contains four atoms (CH_2O), and one of acetic acid eight atoms ($C_2H_4O_2$), and one of dextrose twenty-four atoms ($C_6H_{12}O_6$), although the relative numbers of each kind are the same. Indeed this hypothesis helps to clear the matter up, for chemists go so far as to account for the chemical behavior of the substances by an imagined geometrical arrangement of the atoms in their molecules, and these three kinds of molecules are supposed to differ in structure as well as in the number of atoms they contain.

The Molecular Weights and Formulæ of Elementary Substances. — The following table gives the densities of some elementary substances, including those of which the substances previously discussed are compounds. The first column shows the atomic weight, which in each case is the minimum weight of the element found in a G.M.V. of any *compound*. For example, 16 g. of oxygen and 35.46 g. of chlorine are the weights in the amounts of water vapor and hydrogen chloride, respectively, which fill the cube (22.4 liters). The symbol, in the next column, stands for this quantity and occurs in many formulæ, such as H_2O and HCl. It represents the combining unit or atom. In the third column is given the weight of the *free*, elementary substance which fills the G.M.V. and is the molecular weight. It shows the weight of the molecule relative to the weights of the other molecules in the same column, and to the weights of the atoms in the first column. In the last two columns are given the molecular weights resolved into multiples of the atomic weights and the corresponding formulæ.

Element.	Atomic Weight.	Symbol.	Weight in G.M.V.	Weight in G.M.V. Factorized.	Formula of Free Element.
Oxygen	16.00	O	32.00	2×16.00	O_2
Hydrogen	1.008	H	2.016	2×1.008	H_2
Chlorine	35.46	Cl	70.92	2×35.46	Cl_2
Phosphorus	31.04	P	124.16	4×31.04	P_4
Mercury	200.6	Hg	200.6	1×200.6	Hg
Ozone	16.00	O	48.00	3×16.00	O_3
Cadmium	112.4	Cd	112.4	1×112.4	Cd
Potassium	39.10	K	39.10	1×39.10	K
Sodium	23.00	Na	23.00	1×23.00	Na
Zinc	65.37	Zn	65.37	1×65.37	Zn

The reader cannot fail to note a striking peculiarity. In the case of chlorine the molecular weight is 70.92, while the atomic weight is 35.46. With hydrogen and oxygen, also, the molecular weight contains two atomic weights. Yet this is not a general rule, for with mercury and several other elements the molecular and atomic weights are alike, while with phosphorus the molecular is four times the atomic weight. Evidently there is no rule, and each element has to be subjected to separate experimental study. The result is that for *free, elementary chlorine we use the molecular formula* Cl_2, for *free hydrogen* H_2, for *elementary, uncombined oxygen* the formula O_2. For a substance like phosphorus, which is not a gas and is not often used as a vapor, the formula P is commonly employed by chemists, to avoid the larger coefficients which P_4 introduces into equations, although theoretically the latter formula would be the strictly correct one.

The case of oxygen demonstrates clearly the necessity of using molecular formulæ, even for simple substances. The table shows *two* substances containing nothing but oxygen. Ozone (*q.v.*) has a molecular weight 48, being a gas exactly one-half heavier than ordinary oxygen. Its formula, therefore, is O_3, while that of oxygen is O_2. Oxygen and ozone are entirely different chemical individuals. The latter has, for example, a strong odor and is much more active. Thus polished silver remains bright indefinitely in pure oxygen, but oxidizes quickly when placed in ozone.

To avoid a common error, the reader should note that to learn the *atomic* weight of an element, we do *not* measure the molecular weight of the *simple* substance. The molecular weight of the elementary substance may be a multiple of the atomic weight, and we find out whether it is such a multiple only after the atomic weight has been determined. The atomic weight is the unit weight *used in compounds,* and can be ascertained only by a study of compounds. The molecular weight of the free element gives us only a value which we know must be a multiple of the atomic weight, by 1 or some other integer. Mol. Wt. = At. Wt. × x, where x is 1 or some other integer.

Further Discussion of the Molecular Formulæ of Elementary Substances. — Some further explanation may be required, to the end that the reader may be reconciled to accepting the formulæ Cl_2, O_2, and so forth. In the first place, he should note how these formulæ arose. If we accept Avogadro's law, and the inference from it to the effect that the weights of equal volumes of gases are in the same ratio as the weights of their individual molecules, then we cannot escape the conclusion to which measuring the relative densities of free chlorine and hydrogen chloride, for example, leads. The ratio of their densities is 70.92 : 36.46. That is to say, the relative weights of a molecule of chlorine and a molecule of hydrogen chloride stand in this ratio. The molecule of chlorine is nearly twice as heavy as the molecule of the compound, *and there cannot therefore be a whole* **molecule** *of chlorine in a molecule of hydrogen chloride.* In fact, we perceive at once that the molecule of hydrogen chloride must contain only half a molecule of chlorine (35.46), together with half a molecule of hydrogen (1). In other words, if the molecule of free chlorine were to be taken as the atom of the element, then the molecule of hydrogen chloride would contain only half an atom of chlorine, which would be contrary to our definition to take as atoms quantities which are not divided. So we choose the other horn of the dilemma, and say that the specimen of chlorine in the molecule of hydrogen chloride is a whole atom and that therefore the amount of chlorine in the molecule of free chlorine is two atoms, and its formula Cl_2. Similarly, the weight of hydrogen in the molecule of hydrogen chloride is 1.008, while that of the molecule of hydrogen is 2.016, so that there are two atoms in the molecule of free hydrogen and its formula is H_2. Reasoning in like manner from the molecular weights of oxygen (32) and water (18) we reach the conclusion that the molecule of oxygen is **diatomic** (O_2).

The simple fact that hydrogen and oxygen, when mixed, do not combine (p. 59) may assist in reconciling us to the diatomic nature of their molecules. Some part of the mixture has to be heated strongly to start the interaction. Now the molecular formulæ, H_2 and O_2, suggest that each gas is really in combination already (with itself), and they therefore explain to some extent the indifference of the gases towards one another. If the molecules were free atoms, they could not encounter one another continually as they move about, and yet escape combination as we observe that they do. We may imagine that the primary effect of heating is to decompose some of the molecules, and liberate hydrogen and oxygen in the atomic condition, and that the combination of these atoms starts the explosion of the whole mass.

In the case of hydrogen, the diatomic nature of the molecules has been demonstrated by an entirely different method by Langmuir. It has long been known that the conductivity of hydrogen for heat is greater than that of any other elementary gas. Thus, a wire raised to a white heat in air by means of an electric current, cannot be kept at a red heat, even, by the same current in hydrogen. In other gases, heat from the hot wire is used up in accelerating the motion of the molecules of the gas. Langmuir has shown, however, that in hydrogen, additional heat is consumed in causing decomposition of many of the diatomic molecules into single atoms:

$$H_2 \rightleftarrows 2H.$$

He has measured the percentage of molecules dissociated (at 760 mm.), and found that it varies from 0.33 per cent at 2000° to 13 per cent at 3000° and 34 per cent at 3500°. When the temperature falls, the atoms re-combine to diatomic molecules. It may also assist in making the matter clear if we note that the atomic weight of an element is the unit quantity of that particular variety of matter, *when it is in combination*. The unit quantity of the same variety of matter, when in the free state, as a *substance*, need not be the same. We should not expect it to be smaller, but it might easily be twice or more times as large.

Applications

Applications: Interactions Between Gases. — According to Avogadro's hypothesis, if we filled a succession of vessels of equal dimensions with different gases, and could arrest the motion of the particles and observe their disposition, we should find that the average distance from particle to particle would be the same in all cases. This would be true whether our vessels were filled with single gases, with homogeneous mixtures, or with gases in layers. Such being the case, if any chemical change is brought about in the mass which results in a multiplication of the molecules, it is evident that the volume will have to increase in order that the spacing may remain the same as before. If any chemical action results in a diminution of the number of molecules, then a shrinkage must take place in order that the spacing may be preserved as before. Thus, in a mixture of hydrogen and oxygen, according to our hypothesis, when the interaction occurs, the following change takes place between neighboring molecules:

$$\mathrm{HH + OO + HH} \text{ becomes } \mathrm{HOH + HOH}.$$

Since the oxygen molecules, which form a third of the whole, disappear into the molecules of hydrogen, the tendency to preserve spacing results in a diminution of the volume by one-third (p. 98). Thus Gay-Lussac's law would have followed as a natural inference from Avogadro's law, if the former, being more obvious, had not been discovered first.

If each of the following squares represents a small volume containing 1000 molecules of gas, then 2000 molecules of hydrogen and 1000 molecules of oxygen give 2000 molecules of water vapor. We may note, in passing, that, since each molecule of water must contain at least one atom of oxygen, at least 2000 atoms of oxygen were required, and must have been furnished by the 1000 molecules of oxygen. Each of these molecules must therefore have split into two atoms.

$$\boxed{\begin{array}{c}\text{Hyd.}\\ 1000\\ \text{mols.}\end{array}} + \boxed{\begin{array}{c}\text{Hyd.}\\ 1000\\ \text{mols.}\end{array}} + \boxed{\begin{array}{c}\text{Ox.}\\ 1000\\ \text{mols.}\end{array}} \rightarrow \boxed{\begin{array}{c|c}\text{Aq.} & \text{Aq.}\\ 1000 & 1000\\ \text{mols.} & \text{mols.}\end{array}}$$

This method of looking upon chemical interactions between gases gives us the nearest sight which we can have of the behavior of the molecules themselves. We cannot perceive the individual molecules, but, in consequence of the spatial arrangement which they observe, the change in the whole volume of a large aggregate of molecules enables us to draw conclusions at once in regard to the behavior of the single molecules in detail.

Applications: Molecular Equations. — To utilize the foregoing considerations, chemists **always employ in their equations the molecular formulæ** for the gases and the easily vaporized substances concerned. Thus far, we have used the equation:

	$2H$	$+$	O	$\rightarrow$	H_2O
WEIGHTS:	2×1.008		16		18.016

and the information it contained was exhausted when we had placed below the symbols the weights for which they stood. But the molecular equation is much more instructive. The following shows **the interpretations to which the molecular equation is subject:**

	$2H_2$	$+$	O_2	$\rightarrow$	$2H_2O$
WEIGHTS:	2×2.016 g.		32 g.		2×18.016 (= 36.032) g.
VOLUMES:	2×22.4 l.		22.4 l.		2×22.4 l.
MOLECULES:	2		1		2

The weights, although doubled, show the same proportions, so that questions of weight are answered as easily as before. These weights, however, being molecular weights, or multiples thereof, can be translated at once into *volumes*, and **questions about volumes can also be answered.** Finally, **the relative numbers of each kind of molecules can be read from this equation,** for the coefficients in front of the formulæ represent these numbers. Where no coefficient is written, 1 is to be understood.*

Applications: The Making of Molecular Equations. — To make a molecular equation, we first make an equation according to the rules already explained (p. 51). An equation like that given for the interaction of potassium on water (p. 50): $K + H_2O \rightarrow KOH + H$, is the result. Then we adjust the equation so that molecular formulæ are used throughout. The hydrogen must appear as H_2, or a multiple of this, in such equations. Hence the whole equation must be multiplied by 2:

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* The application of these properties of molecular equations is illustrated in Chap. XI (pp. 149–153). If desired, these applications may be taken up after the next section.

$$2K + 2H_2O \rightarrow 2KOH + H_2.$$

Again, the equation for the preparation of oxygen from potassium chlorate: $KClO_3 \rightarrow KCl + 3O$ (p. 27), becomes:

$$2KClO_3 \rightarrow 2KCl + 3O_2.$$

Every equation containing an *odd* number of atoms of a substance whose molecules are *diatomic* must be multiplied by 2. Again, mercuric oxide decomposes to give mercury vapor and oxygen (p. 14), and the molecules of mercury are monatomic and those of oxygen diatomic, so we write:

$$2HgO \rightarrow 2Hg + O_2.$$

Finally, the formulæ of substances which are solid or liquid, and cannot be easily vaporized, are written in the simplest terms. Thus, since substances like the copper in the following equation are involatile, the molecular weights of such substances are unknown, and their molecular formulæ likewise: $2Cu + O_2 \rightarrow 2CuO$. Furthermore, in the case of substances which can be volatilized, although the molecular weights and molecular formulæ may therefore be known, we do not usually employ the molecular formulæ if the substance is not used in the form of vapor in the laboratory. Thus, the molecular formula of phosphorus pentoxide is P_4O_{10} (p. 105). But we generally make, and use, only the solid form, and not the vapor, in actual work. Hence the action with water is usually written as we have given it (p. 94), rather than in the form: $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$.

Molecular equations will be used exclusively hereafter.

Applications: To Cases of Dissociation. — Several gases or vapors yield smaller values for their densities, and therefore molecular weights, when the densities are measured at higher temperatures. This indicates that the molecules have become lighter, and can only mean that decomposition has taken place in consequence of the heating. Behavior of this kind is shown both by compounds and by simple substances.

For example, phosphorus pentachloride PCl_5, although a solid, can be converted into vapor without much difficulty. Its molecular weight, if it underwent no chemical change during the volatilization, would be 31 + 177.3 = 208.3. The density actually observed at 300° and 760 mm. pressure gives by calculation not much more than half this value. The direct inference from this is that the molecules have only half the (average) weight that we expected; or, in other words, are twice as numerous as we expected. The explanation is found when we examine the nature of the vapor more closely. We find that it is a mixture of phosphorus trichloride and free chlorine, resulting from a chemical change according to the equation: $PCl_5 \rightleftarrows PCl_3 + Cl_2$. The low value of the density thus tells us that dissociation has taken place. From the value of the density at various temperatures, we may even calculate the proportion of the whole material which is dissociated. At 300° it is 97 per cent; at 250°, 80 per cent; and at 200°, 48.5 per cent. Thus, when the temperature is lowered, progressive recombination takes place and the proportion dissociated becomes less. Finally the vapor condenses and yields the original solid.

Again, sulphur boils at 445°, but can be vaporized at a temperature as low as 193°, under very low pressure. At this temperature the density of the vapor gives the molecular weight 256 (= 8 × 32), and the molecular formula S_8. That is to say, the G.M.V. holds 256 g. of the vapor at 193°. At 800°, however, the density is only one-fourth as great, and the G.M.V. holds only 64 g. (S_2). This means that 256 g. now occupy four times as large a volume as before, *and the increase is additional to the effect of the mere thermal expansion*, which is allowed for in the calculation and eliminated. Hence the molecules have dissociated. At 1700° the molecular formula is still S_2, so that this represents the limit of dissociation: $S_8 \rightleftarrows 4S_2$. When the vapor is cooled, the density increases once more and at 193° recovers completely the greater value. Similar observations show that phosphorus vapor at 313° is all P_4, but at 1700° one-half of the molecules are P_2. Iodine vapor, up to 700°, is all I_2. Beyond this temperature the density diminishes, and when 1700° is reached the vapor is all I. Thus the molecules are diatomic at low temperatures and monatomic at high ones. The densities of oxygen, hydrogen, and chlorine are not measurably affected by heating to 1700°, so that their diatomic molecules exist from temperatures far below 0° up to 1700°, and are evidently very stable. For observations on hydrogen above 1700°, however, see p. 113.

Applications: Finding the Atomic Weight of a New Element. — By way of reviewing the principles explained in this chapter, let us apply them to the imaginary case of a newly discovered element. The bromide of the element is found to be easy of preparation and to be volatile. The bromide contains 30 per cent of the element (and therefore 70 per cent of bromine), and its vapor density referred to air is 11.8. The analysis can always be made much more accurately than the measurement of vapor density, so that the former number is more trustworthy than the latter.

To find the equivalent of the element, that is, the amount combined with 79.92 parts (the atomic weight) of bromine, we have the proportion 70 : 30 :: 79.92 : x, from which $x = 34.3$. The atomic weight must be this, or some small multiple of it.

The G.M.V. of air weighs 28.955 g. (p. 101). Hence the same volume of the vapor of this bromide, which is 11.8 times as heavy as air, will weigh 28.955 × 11.8, or 341.67 g. This is therefore the molar weight of the compound.

Now 30 per cent of this is the new element:

$$341.67 \times 30 \div 100 = 102.5.$$

Now 34.3 parts of the element combined with 79.92 parts of bromine. Evidently the atomic weight of the element is $3 \times 34.3 =$ **102.9**, the difference being due to error in determining the density. So long as no other volatile compound is known, we adopt this as the atomic weight. The rest of the molar weight (239 parts = 3 × 79.92) is bromine. Thus the formula of the compound is $ElBr_3$, and from this we see that the element is **trivalent.**

In case no volatile compound of the element can be formed, the weight combining with 79.92 parts of bromine is measured as before. Then some of the free simple substance is made, say by electrolysis, and its specific heat is determined. The sp. ht. is about 0.063. Application of Dulong and Petit's law then gives the atomic weight. The product 34.3 × 0.063 is equal to 2.161. Hence, the equivalent must be multiplied by 3 to give the atomic weight, for this raises the product to 6.48, which is within the limits. Thus the value of the atomic weight is 102.9, as before.

Replies to Questions about Difficulties. — The beginner always becomes confused over one or more of the points raised by the following questions:

1. Why was 32 g. of oxygen taken as the standard for molecular weights, rather than 16 g.? Read p. 107 and footnote to p. 104.
2. If O_2 is the smallest mass of oxygen, why do we have formulæ like H_2O and HClO? O_2 is the smallest mass of *free* oxygen, but in combination half as much occurs in many molecules. Read pp. 105, 110, and 111.
3. Why is not the atomic weight of an element ascertained by simply measuring the density of the elementary substance? Read pp. 111, last par., and 117, second par.
4. Can we not deduce the valence of an element from knowing the number of atoms in its molecules, and *vice versa?* Some molecular formulæ and valences are: $H_2{}^{I}$, $O_2{}^{II}$, $Cl_2{}^{I}$, Zn^{II}, also Hg (univalent and bivalent), P_4 (trivalent and quinquivalent), and S_8 (bivalent and sexivalent). There is no relation, either observable or to be expected.
5. Do the molecular weights, oxygen = 32 and hydrogen = 2, mean that the molecules of oxygen are *larger* than are those of hydrogen? This is the ratio of their weights, but none of the phenomena discussed in this chapter are influenced appreciably by their relative sizes, and therefore none of them give any information on the subject. Read the footnote to p. 102.

Exercises. — 1. The weight of 1 l. of a gas at 0° and 760 mm. is 5.236 g. What is the density referred (*a*) to air (air = 1) and (*b*) to hydrogen, and (*c*) what is the molecular weight (pp. 101, 102)?

2. The density of a gas, referred to air, is 6.7. What is the weight of 1 l. (p. 101), and what is the molecular weight (p. 118)?

3. The molecular weight of a substance is 65. What is the density referred to air, and what is the weight of 1 l.?

4. The chloride of a new element contains 38.11 per cent of chlorine and 61.89 per cent of the element. The vapor density of the compound referred to air is 12.85. What is the atomic weight

of the element, so far as investigation of this one substance can give it (p. 118)? What is its valence?

5. If the molecular weight of oxygen were taken as 100, what would be the volume of the G.M.V. (p. 101)? What, on the same scale, would be the molecular weight of water, and what would be the atomic weights of hydrogen and chlorine (pp. 101, 105)?

6. In future nothing but molecular formulæ of free elements must be used (p. 111). Write in molecular form ten of the equations involving gases which are found in the preceding chapters.

7. If a new form of oxygen were found, such that one volume of it required four volumes of hydrogen to produce water, what would be its molecular formula (p. 114)? What would be the weight of 22.4 l.?

CHAPTER X

SOLUTION

SOLUTIONS are so constantly used in chemistry that some knowledge of their properties is desirable in order that we may employ them intelligently. In what follows, we give a preliminary account of some of the simpler facts about solution.

General Properties of Solutions. — A *solid* may be distributed through a liquid, either by being simply suspended (p. 12) in the latter (mixture), or by being dissolved in it (solution). Similarly a *liquid* may be suspended in droplets in another liquid (**emulsion**), as in milk, or it may be dissolved. It is usually easy to distinguish between the two cases, for a suspended substance *settles* or separates sooner or later (like the fats in milk — as cream), while a dissolved substance shows *no such tendency*. The cases are exceptional where the subdivision of a suspended substance is so minute (**colloidal suspension,** *q.v.*), as to make its retention by filter paper impossible. If a liquid is opalescent or opaque, then we have a case of suspension. A solution is a clear, transparent, perfectly homogeneous liquid, in which the dissolved substance seems to have been dispersed so completely that the liquid cannot be distinguished by the eye from a pure substance.

There is no limit to the amount of dissipation which may thus be produced. A single fragment of potassium permanganate, for example, which gives a very deep purple solution in water, may be dissolved in a liter or even in twenty liters of water, and the purple tinge which it gives to the liquid will still be perfectly perceptible in every part of the larger volume. **The qualitative characteristics,** therefore, **of solution** are **absence of settling, homogeneity, and extremely minute subdivision of the dissolved substance.**

The Scope of the Word. — The word solution is used for other systems than those containing a solid body dissolved in a liquid.

Thus, liquids also may be dissolved in liquids, as alcohol in water. Again, if we warm ordinary water, bubbles of gas appear on the sides of the vessel before the water has approached the boiling-point. They are found to be gas derived from the air. Agitation of any gas with water results in the solution of a large or small quantity of the gas, and heat will usually drive the gas out again. It appears therefore that **solids, liquids,** and **gases** can equally **form solutions in liquids.**

The absorption of hydrogen by palladium (at all events after a certain point), and by iron, takes place in accordance with the same laws as the solution of solids in liquids, and the results may be described therefore as true solutions. Liquids are in some cases absorbed by solids, and homogeneous mixtures of solids with solids are perfectly familiar. The sapphire is a solution of a small amount of a strongly colored substance, in a large amount of colorless aluminium oxide. It may therefore be stated that **solution of gases, liquids,** and **solids in solids** appears to be possible.

Limits of Solubility. — The next question which naturally occurs to us is as to whether the mingling of two substances in this manner has any limits. We find that the results of experiment in this direction may be divided into two classes. Some pairs, of liquids particularly, may be mixed in any proportions whatever. Alcohol and water, and glycerine and water are such pairs. On the other hand, at the ordinary laboratory temperature, we can scarcely take a fragment of marble ($CaCO_3$) so small that it will dissolve completely in 100 c.c. of pure water, for only 0.00013 g. dissolves. Under the same conditions any amount of potassium chlorate up to about 5 g. will completely disappear after vigorous stirring, while 90 g. of ordinary Epsom salts (hydrated magnesium sulphate), but not more, may be dissolved in about the same amount of water. In fact, most solids may be dissolved in a liquid only up to a certain limit, which with different solids may range from a scarcely perceptible to a very large amount. No substance is absolutely insoluble. But for the sake of brevity we call marble, for example, "insoluble" because in most connections it may be so considered.

Chemists have not yet succeeded in explaining these differences in solubility, which are often so surprising. Thus, guncotton is soluble in a mixture of alcohol and ether, but not in these liquids separately, while cellulose acetate (an allied substance, used in making artificial horse-hair) is soluble in these liquids separately, but not in the mixture.

Recognition and Measurement of Solubility. — The only method of **recognizing** with certainty whether a solid is soluble in a liquid or not is to filter the mixture and evaporate a few drops of the filtrate on a clean watch-glass. For learning **how much** of the body is contained in a given solution, a weighed quantity of the solution is evaporated to dryness and the weight of the residue determined.

It must be stated explicitly that in going into *solution*, as we have used the term, a compound dissolves as a whole and, if the compound is pure (p. 4), any residue has the same chemical composition as the part which has dissolved. If the residue is a different substance, a chemical interaction with the solvent has occurred. If, on evaporation, a different substance remains, there has also been chemical action.

Terminology. — In order to describe the relations of the components of a solution, certain conceptions and corresponding technical expressions are required.

It is customary to speak of the substance which, like water in most cases, forms the bulk of the solution, as the **solvent.** To express the substance which is dissolved, the word **solute** is frequently used, and will be employed when we wish to avoid circumlocution.

The amount of the substance which has been dissolved by a given quantity of the solvent is described as the **concentration** of the solution. A solution containing a small proportion of the dissolved body is called **dilute;** it has a small concentration. One which contains a larger amount is **more concentrated.** Very "strong" solutions are frequently spoken of simply as **concentrated solutions.** The *partial* removal of the solvent (as by evaporation) is called **concentrating,** its total removal **evaporating to dryness.**

Finally, since there is a limit to the solubility of most substances, a solution is described as **saturated** when the solute has given as much material to the solvent as it can. This state is reached after prolonged agitation with *an excess* of the gas, of the liquid, or of the *finely powdered* solid, as the case may be (see pp. 127, 133). Other things being equal, the larger the excess, the sooner saturation is attained. The maximum concentration attainable in this way is called the **solubility** of the substance in a given solvent. Note that a saturated solution need not also be a concentrated one. It will be very dilute, if the solute is but slightly soluble.

Units Used in Expressing Concentrations. — The concentrations of solutions, saturated and otherwise, are sometimes expressed in physical, and sometimes in chemical, units of weight. When **physical units** are employed, we give the number of grams of the solute held in solution by one hundred grams of the solvent.

The **solubilities** at 18° of **one hundred and forty-two bases and salts** are given in a **table** printed **inside the cover, at the front of this book.**

When **chemical units** of weight are employed, two different plans are possible, and both are in use. Either the equivalent (p. 65) or the molecular weights may be taken as a basis of measurement. In the former case, the solutions are called **normal solutions,** and in the latter, **molar solutions.**

A normal solution contains one gram-equivalent of the solute in one liter of solution (*not* in 1 l. of solvent). The word "equivalent" has been used hitherto only of elements, and this application of the expression involves an extension of its meaning. **An equivalent weight of a compound is that amount of it which will interact with one equivalent of an element.** Thus, a formula-weight of hydrochloric acid HCl (36.5 g.) is also an equivalent weight, for it contains 1 g. of hydrogen, and this amount of hydrogen is displaceable by one equivalent weight of a metal. A formula-weight of sulphuric acid H_2SO_4 (98 g.), however, contains two equivalents of the compound, and a formula-weight of aluminium chloride $AlCl_3$ (133.5 g.) three equivalents. Hence normal solutions of these three substances contain respectively 36.5 g. HCl, 49 g. H_2SO_4, and 44.5 g. $AlCl_3$ per liter of solution. The special property of normal solutions is, obviously, that equal volumes of two of them contain the exact proportions of the solutes which are required for complete interaction. Solutions of this kind are much used in quantitative analysis. We frequently use also decinormal or one-tenth normal solutions (0.1 N or $N/10$), and seminormal (0.5 N or $N/2$), and six times normal solutions (6 N), and so forth.

A molar solution contains one mole (gram-molecular weight) of the solute in one liter of solution (*not* in 1 l. of solvent). When molecular formulæ (p. 109) are used, this means one gram-formula weight per liter. In the cases cited above, the molar solution contains 36.5 g. HCl, 98 g. H_2SO_4, and 133.5 g. $AlCl_3$ per liter. As will be seen, the concentrations of molar and normal solutions are necessarily identical when the radicals are univalent.

Solution One of the Physical States of Aggregation of Matter. — When a solid body dissolves in a liquid, the properties of the body undergo a very marked change, which to all appearance might be chemical. Yet, besides the ease with which a liquid may be removed by evaporation and the solid recovered unchanged, we note particularly that the concentration of a saturated solution cannot be expressed in terms of integral multiples of the atomic weights. We shall see also that the quantity of a solid which a liquid may take up varies with the slightest change in temperature. Now we do not find the composition of chemical compounds so to vary. The solution of a solid may therefore, in general, be likened to a change in state of aggregation, similar to the conversion of a liquid into a gas or a solid (see p. 126).

As in other changes of state, so in the process of solution, heat is always liberated or absorbed. This is known as **heat of solution.** Thus, one formula-weight of sulphuric acid, in dissolving in a large volume of water, liberates 39,170 calories, and one formula-weight of ammonium chloride, in dissolving, *absorbs* 3880 calories.

As there is danger of confusion arising, we may repeat that a compound is homogeneous and its composition is expressible in chemical units of weight; a saturated solution is homogeneous but its concentration varies with temperature so that atomic weights cannot be used to describe its composition; a mixture of two solids, or an emulsion of two liquids, is neither homogeneous nor in any way definite in composition.

Molecular View of the State of Solution. — Accepting solution as a physical state of aggregation, we may now apply the same molecular conceptions to the explanation of the behavior of a substance in solution as to matter in the gaseous or liquid states. We saw that a solid body, which is ordinarily condensed in a small space, can be disseminated by the use of a solvent through a very large one. The molecules of the solid become scattered like those of a gas or vapor through a much greater volume. We may regard the dissolved substance as being, practically, in a gaseous or *quasi*-gaseous condition. The molecules are torn apart from one another, their cohesion is overcome, and their freedom of motion is in a measure restored. It is true that they could not continue to occupy this large volume for a moment in the absence of the solvent. But we may bring this into relation with the case of a vapor by saying that a solid body, like common salt, can evaporate (*i.e.*, "dissolve") at the ordinary temperature, and occupy a large space, only when that space is already filled with a suitable liquid. The latter acts as a vehicle for the particles of the solid. A volatile liquid, on the contrary, can dissolve in an *empty* space and fill it with its particles without any vehicle being required.

This conception of the *quasi*-gaseous condition of a dissolved substance would be simply fantastic if it did not lead us to a better understanding of the behavior of solutions. It does successfully explain many things, such as diffusion, osmotic pressure, and saturation (see next section).

It is easy to show that, if we place a quantity of the pure solvent (Fig. 55) above a concentrated solution of a substance, and then set the arrangement aside, the dissolved body slowly makes its way through the liquid (Fig. 56), obliterating the original plane of separation. Eventually the dissolved body scatters itself uniformly through the whole. In other words, the particles of the dissolved substance exhibit the property of **diffusion** in the same way as do those of gases.

When the diffusion of a *gas* is resisted by a suitable partition, we find that pressure is exercised upon the walls of the vessel and upon the partition. It is possible to show that the particles of a *dissolved substance* exercise a pressure of a very similar kind. This pressure is spoken of as **diffusion pressure.** This pressure is found to be proportional to the concentration of the solution, just as gaseous pressure is proportional to the concentration of the gas (Boyle's law).

Molecular View of the Process of Solution. — We may now apply the same ideas to the process of dissolving, with a view more especially to explaining why this process ceases, in spite of the presence of excess of the solute, when a certain concentration has been reached. If some of the material dissolves, why not more?

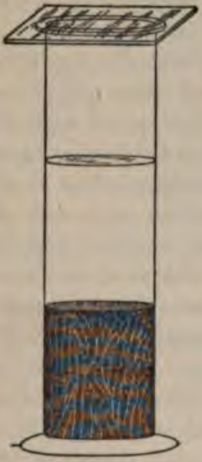


Fig. 55.

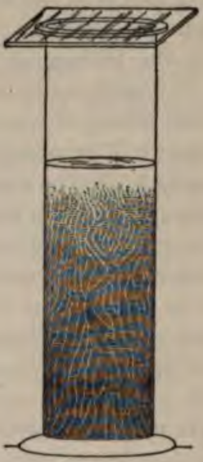


Fig. 56.

Let us suppose that it is the dissolving of common salt in water (Fig. 57) which we wish to explain in detail. We believe that in the solid substance the molecules are closely packed together, while in the solution they are rather sparsely distributed. The process of solution must consist in the loosening of the molecules on the surface and their passage into the liquid. By diffusion, the free molecules will gradually move away from the neighborhood of the surface of the solid and make room for others, and thus, if the system remains undisturbed, the liquid will eventually become a solution of uniform concentration. If a large enough amount of the solid has been provided, the ultimate condition will be that of a saturated solution with excess of the solid

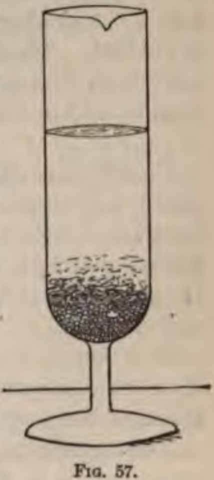


Fig. 57.

beneath. If we had proper means of measuring it, the tendency of the molecules to leave the solid in the presence of a given liquid would give the effect of a kind of pressure. This is spoken of as **solution pressure.**

Now the molecules, after having entered the liquid, move in every direction, and consequently some of them will return to the solid and attach themselves to it. The frequency with which this will occur will be greater as the crowding of particles in the liquid increases, so that a stage will eventually be reached at which the number of molecules leaving the solid will be no greater than that landing upon it in a given time. If the whole of the liquid has meanwhile become equally charged with dissolved molecules, there will be no chance that the field of liquid immediately round the solid will lose them by diffusion, so that a condition of balance or equilibrium (p. 89) will have been established: NaCl (solid) $\rightleftarrows$ NaCl (dslvd). The motion of the particles in the liquid produces what we have called diffusion pressure; and *when the diffusion pressure*, by the continual increase in the number of dissolved molecules, *becomes equal to the solution pressure*, increase in concentration of the solution ceases. It is at this point that *we speak of the solution as being saturated* with respect to the particular substance dissolving. The analogy to vapor tension and vapor pressure (p. 88) is evident. The foregoing explanation should be compared carefully with that given in the section on the molecular relations in liquids, and in that on equilibrium (pp. 81, 89–90).

Conditions Affecting the Solubility of a Gas. — When the dissolving substance is a **gas,** led through, or confined above the liquid at a definite pressure, the gas dissolves until a state of equilibrium between dissolving and emission is reached, for example, Oxygen (gas) $\rightleftarrows$ Oxygen (dslvd), and the liquid is then saturated with the gas.

It is found, as the molecular theory would lead us to expect, that **the concentration of the saturated solution of a gas is proportional to the pressure at which the gas is supplied** (**Henry's law**).

This equilibrium, Gas (gaseous) $\rightleftarrows$ Gas (dslvd), can be reached, naturally, from the other direction, namely by starting with a solution of the gas and a space above the solution containing, at first, none of the gas. The gas leaves the solution until the rates of emission and return become equal. Hence, a gas may be entirely removed from solution by bubbling a foreign gas through the liquid. The bubbles furnish the space to receive the emitted gas, and have a large surface, so that the process goes on rapidly. The bubbles also escape, and carry with them the emitted gas, so that, in this case, there is no re-solution. This is a case of nullifying one of the two opposed tendencies (p. 90).

When a **mixture of two gases** is shaken with a liquid, the gases behave independently of each other (Dalton's law, p. 72). Each has the same pressure, and therefore the same solubility, as it would possess if it alone occupied the *whole* space above the liquid.

Two Immiscible Solvents: Law of Partition. — An interesting application of the same ideas may be made to a case which occurs very commonly in chemical work. If we shake up a small particle of iodine with water, we find that it dissolves slowly, giving eventually a saturated but very dilute solution. If now ether in sufficient quantity be shaken with the aqueous solution, the greater part of the iodine will find its way into the ether, and be contained in the brown layer which rises to the top. The process of removing a substance partially from solution in one solvent and securing it in another is called **extraction.** We find in such cases that neither solvent can entirely deprive the other of the whole of the dissolved substance, if the latter is soluble in both independently. A state of equilibrium is finally reached: I_2 (in Aq) $\rightleftarrows$ I_2 (in ether). The partition of the substance takes place in proportion to its solubility in each solvent. It is found that any amount of the solute, up to the maximum the system can contain, provided this does not involve too high a concentration in either solvent, is divided so that the ratio of the concentrations in the two solvents is always the same. In the case of iodine divided between water and ether, this ratio is about 1 : 200.

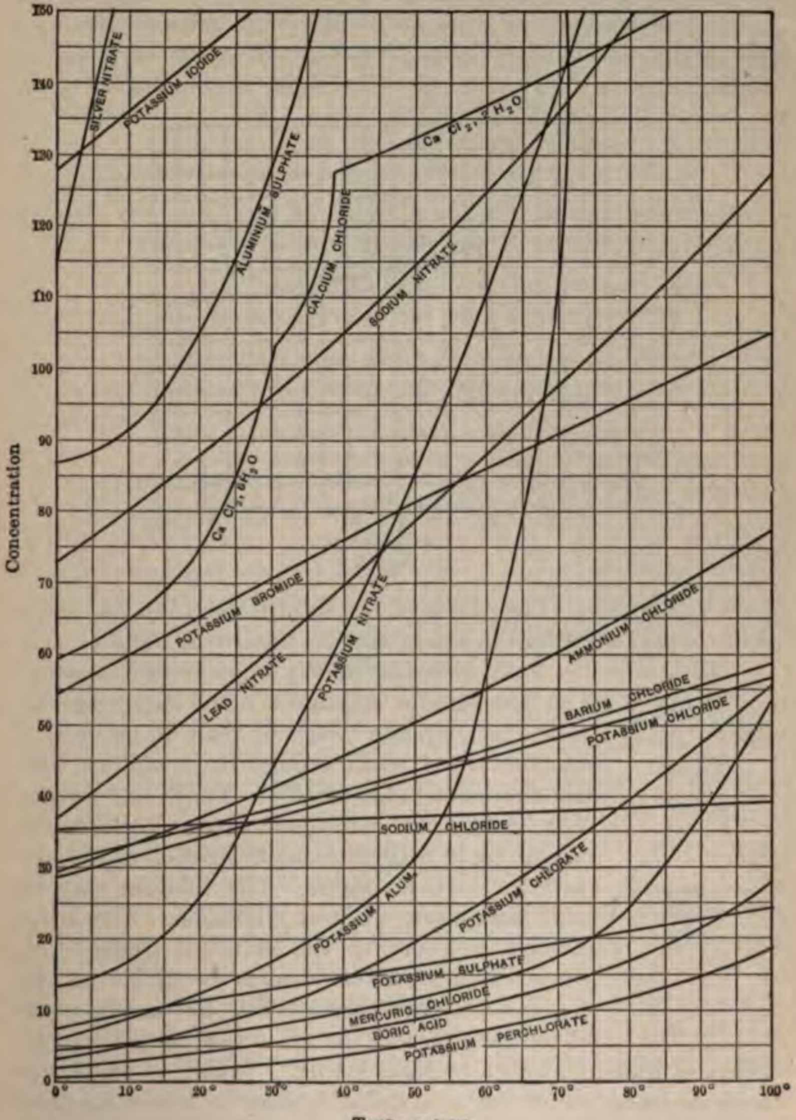
This principle is used in Parke's process (*q.v.*) for extracting silver from molten lead, by means of melted zinc as the second solvent. It is employed in separating interesting compounds from animal secretions and vegetable extracts, and in purifying such compounds. Nicotine from tobacco and cocaïne from coca-leaves, are secured in this way.

Influence of Temperature on Solubility. — The quantity of a substance which we can dissolve in a fixed amount of a given solvent depends very largely upon the temperature of both. Usually the solubility increases with rise in temperature. Measurements may be made by the method described before (p. 123), using *excess* of the finely powdered solute with different portions of the same solvent in vessels kept at different temperatures. The most useful way of representing the results is to plot them graphically. The diagram (Fig. 58) shows the curves for a few familiar substances. The ordinates represent the number of grams of the anhydrous compound which is held in solution by 100 g. of water in each case. The abscissæ represent the temperatures. The concentration for any temperature can be read off at once. Thus, 100 g. of water holds 13 g. of potassium nitrate in solution at 0° and 150 g. at 73°. The increase in solubility is here enormous. On the other hand, the same quantity of water will hold 35.6 g. of sodium chloride in solution at 0° and 39 g. at 100°. The difference is shown at once when we examine the curves and observe that the line representing the solubility of sodium chloride scarcely rises at all between 0° and 100°, while that of potassium nitrate is extremely steep.

Cases in which the solubility decreases with rise in temperature are less common. The solubility of slaked lime (calcium hydroxide $Ca(OH)_2$, used to make limewater) is 0.175 g. at 20° and 0.078 g. at 100°. Anhydrous sodium sulphate Na_2SO_4 (Fig. 59, p. 132) is another illustration.

Equilibrium in a Saturated Solution. — Once a solution has become saturated, the dissolving substance remains thereafter unchanged in *amount*. A *greater* excess of the solute forces no more matter into solution than does a small excess.

It should be clearly understood, however, that an exchange of molecules (p. 128) is still going on between the solid and the solution. That this conception is correct may be shown in various ways. Thus, if a crystal, the edges or corners of which have been broken, is suspended in a saturated solution of the same substance, it neither increases nor diminishes in weight. Yet we find that the imperfections are removed, and that this takes place by the solution of a portion of the substance from the perfect surfaces and its deposition upon the imperfect ones.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40°
50°
60°
70°
80°
90°
100°
Concentration
Temperature
SILVER NITRATE
POTASSIUM IODIDE
ALUMINIUM SULPHATE
CALCIUM CHLORIDE
Ca Cl$_2$, 2 H$_2$O
SODIUM NITRATE
Ca Cl$_2$, 6 H$_2$O
POTASSIUM BROMIDE
LEAD NITRATE
POTASSIUM NITRATE
AMMONIUM CHLORIDE
BARIUM CHLORIDE
POTASSIUM CHLORIDE
SODIUM CHLORIDE
POTASSIUM ALUM
POTASSIUM CHLORATE
POTASSIUM SULPHATE
MERCURIC CHLORIDE
BORIC ACID
POTASSIUM PERCHLORATE

Fig. 58.

Supersaturated Solutions. — Another very striking proof of this may be obtained by saturating water with ordinary Glauber's salt (hydrated sodium sulphate $Na_2SO_4,10H_2O$) at, say, 30°, at which temperature 100 c.c. of water hold in solution 40 g. of Na_2SO_4 (Fig. 59). The excess of the solid is carefully and completely separated from the liquid, and the latter is allowed to cool, say to 15°, in a flask loosely stoppered with cotton. The solution now contains a much larger amount of sodium sulphate (Na_2SO_4) than at its present temperature it could acquire from contact with Glauber's salt (13 g. at 15°). Yet in the absence of a crystal, with which the above described exchange could take place, no deposition of the dissolved substance begins. The solution may be kept indefinitely without alteration. The introduction, however, of the minutest fragment of the decahydrate at once starts the exchange, and this is necessarily very much to the disadvantage of the solution and the advantage of the crystal: $10H_2O + Na_2SO_4$ (dslvd) $\rightleftarrows$ $Na_2SO_4,10H_2O$ (solid). The latter therefore forms the center of a radiating mass of blade-like processes, which sprout with astonishing rapidity through the liquid (Fig. 60).

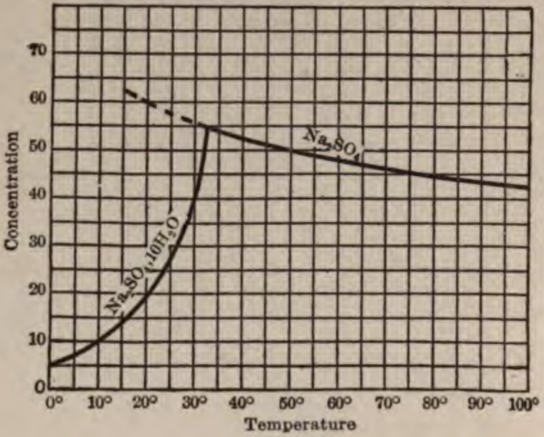

Fig. 59.

Fig. 60.

Usually the cooling of a concentrated solution leads to the almost immediate appearance of crystals spontaneously, and the substance is deposited gradually as the temperature falls. But solutions of a number of common substances, such as sodium thiosulphate (photographer's "hypo") and sodium chlorate, behave like that of sodium sulphate. They are said to have a tendency to give **supersaturated solutions.** In general, crystallization can be started only by introduction of a specimen of the same substance. The smallest particle of the right material floating in the air, if it gains admission, will bring about the result. This shows the importance of the interchange of molecules, of which we have spoken, for establishing equilibrium.

This phenomenon is similar to the supercooling of water (p. 86), which results in crystallization (freezing) when a fragment of ice is dropped in.

Definition of a Saturated Solution: A Warning.—To avoid a common **misconception,** it must be noted that a saturated solution must *not* be defined as one containing all of the solute that it *can hold.* A supersaturated solution holds more. The **saturated solution** is one which contains all of the dissolved solute that it can acquire from the undissolved solute. Better still, it is **that solution which, when placed with excess of the solute, is found to be in equilibrium.**

It must be clearly understood that solution is *not* a process of filling the pores of the liquid. If that were true, approximately equal weights of all substances would find accommodation in equal volumes of water. The fact is that, for example, 100 c.c. of water can dissolve 195 g. of silver fluoride, but only 0.00000035 g. of silver iodide, although the space available in the solvent (if there *is* any free space) is the same in both cases.

The same conclusion is reached when we consider that two forms of the *same compound* have *different* solubilities. Thus, at 20°, $Na_2SO_4,10H_2O$ can give about 18 g. of Na_2SO_4 to 100 c.c. of water (Fig. 59). But *anhydrous* sodium sulphate Na_2SO_4 at 20° gives 59 g. to the same amount of water (read up to dotted line, Fig. 59). Note that in the diagram (Fig. 59) the solubility curve of $Na_2SO_4,10H_2O$ comes to an end at 32.4°. At this temperature the solid melts and decomposes, so that measurements with this solid beyond that temperature are impossible.

Influences of the Solute Upon the Solvent. — These influences are of two classes. In one of these classes, equal numbers of dissolved molecules of different substances produce the *same* amount of change. The effect appears, therefore, to be largely due to mechanical causes. Of this nature are the lowering of the freezing-point of the liquid, the lowering of its vapor tension and the raising of its boiling-point, and the value of the osmotic pressure (see below).

In the other class, the effect varies with the substance dissolved. The changes in volume (see below) belong to this class.

Freezing-Points of Solutions: Freezing Mixtures. — The freezing of a dilute solution consists, usually, in the crystallization of some of the *pure solvent* only. The presence of a dissolved body tends to prevent this freezing, and so solutions can be frozen only at temperatures *below* those at which the pure solvent would freeze. Thus, one gram-molecular weight of any* substance, such as sugar (342 g.) or alcohol (46 g.), dissolved in 1000 c.c. (1 liter) of water, will cause the water to freeze at −1.86° instead of at 0°.

This explains why sea water is much less often frozen in cold weather than is fresh water. It should be noted, also, that the ice formed in salt water is free from salt.

This fact likewise explains why salt thrown on ice causes the latter to melt. A saturated solution of salt does not freeze until cooled to −21° (−6° F.), and it then gives a *mixture* of pure ice and pure salt crystals. Hence, ice and salt cannot permanently exist together *above* −21°. Below −6° F., salt will no longer melt ice. A mixture of ice and salt, giving a temperature of −6° F., is called a **freezing mixture,** and is used in freezing ice cream and ices.

Molecular weights of non-volatile substances can be **measured** by simply finding out what weight of the substance, in 1000 c.c. of water, is required to lower the freezing point from 0° to −1.86°.

The Vapor Tension of Solutions: Deliquescence. — A solute, which is itself non-volatile, tends to diminish the vapor tension of the solvent. It hinders the emission of vapor.

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* For important exceptions, see Chap. XVI.

If the substance is very soluble, and the solution highly concentrated, the lowering in the vapor tension will be considerable. In fact, the solution may give a vapor pressure of water less than that commonly present in the atmosphere. Such a solution, placed in an open vessel, will not evaporate. On the contrary, vapor from the air will enter it, and it will increase in bulk. For this reason, crystals of very soluble substances are usually moist and, when exposed to the air, acquire water from the latter and dissolve in this water. This behavior is called **deliquescence,** and is exhibited, for example, by the hydrate of calcium chloride $CaCl_2,2H_2O$, which is consequently used for drying gases. Magnesium chloride $MgCl_2$, present as an impurity in common salt, causes the latter to become moist in damp weather.

The principle involved will become clear if we imagine two vessels, one containing pure water and one an aqueous solution, to be placed on a glass plate and covered by a bell jar (Fig. 61). Each liquid exchanges water molecules with the moist air in the jar, but the solution gives off water more feebly than does the pure water. The result is that the latter can produce a pressure of water vapor higher than that which would be in equilibrium with the solution. The solution, therefore, receives continuously more molecules than it emits, and increases in volume. The pure water thus gradually passes through the vapor state into the solution until it is all gone. If sufficient water was present, the process would go on until the solution became infinitely dilute.

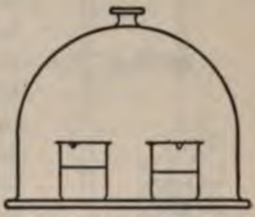

FIG. 61.

Boiling-Points of Solutions. — Since the solute interferes with the emission of the vapor of the solvent, it naturally makes the solution more difficult to boil. It *raises the boiling-point.* Thus one gram-molecular weight of sugar (342 g.) or of glycerine (92 g.), dissolved in 1000 c.c. of water, will elevate the boiling point from 100° to 100.52° (for exceptions, see Chap. XVI).

The Laws of Osmotic Pressure. — We have seen that a dissolved substance exercises a pressure, called osmotic pressure, which is proportional to the concentration of the solute in the solvent. This pressure shows itself when a membrane opposes the diffusion of the solute from the solution into a layer of pure solvent. The phenomena can be illustrated by using a diffusion shell, of test-tube form, attached at the lower end of a glass tube (Fig. 62). We may place the solution (*e.g.*, of sugar) inside the shell, and pure water outside. The material of the shell is such that the water can pass through it in either direction, but the molecules of the dissolved substance cannot do so. Such a membrane is called **semi-permeable.**

The facts observed with this arrangement are as follows: (1) **The pure solvent passes into the solution.** Thus, if the solution is inside the shell, water enters through the wall of the shell, and the liquid therefore *rises* in the tube. If the solution is outside, water passes out of the shell, and the liquid in the tube falls. (2) If solutions of different concentrations are used inside and outside, **the solvent passes from the more dilute into the more concentrated solution,** so that the tendency is to dilute the latter and concentrate the former until both have the same concentration. (3) **The entrance of the solvent can be prevented by the application of pressure to the surface of the liquid in the tube.** With 1 per cent sugar solution inside and water outside (at 15°), a pressure equal to 500 mm. of mercury (0.66 atmos.) per square centimeter of the surface of the membrane is required to stop the entrance of the solvent. This, therefore, is the value of the so-called osmotic pressure. Since the entrance of the solvent is due to the dissolved substance, and the solvent is really **drawn forcefully into the solution,** it might be more appropriate to call the force *osmotic suction.* Whatever it is named, however, it is real, and its value can be measured. (4) **The value of the pressure** (or suction) **increases in proportion to the absolute temperature,** just like the pressure of a gas. (5) **The value of the pressure** (or suction) **is also propor-**

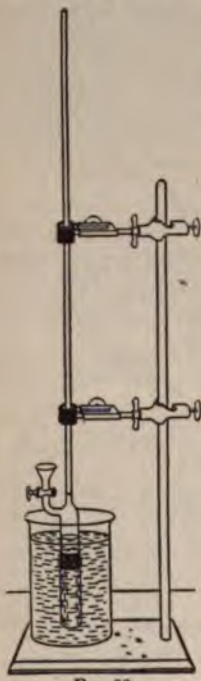
FIG. 62.

tional to the concentration of the solute in the solution. Thus, 2 per cent sugar gave (Pfeffer) 1016 mm. pressure, 4 per cent sugar 2082 mm. (6) When different solutes are compared, it is found that, **at the same temperature, equal numbers of molecules of the solutes dissolved in equal volumes of the solvent give almost equal osmotic pressures** (or suctions). Thus, one mole (342 g.) of sugar $C_{12}H_{22}O_{11}$ and one mole (74 g.) of methyl acetate $CH_3CO_2CH_3$, which, in spite of the great difference in weight, contain equal numbers of molecules, when dissolved separately, each in ten liters of water, give in both cases 2.42 atmospheres osmotic pressure (or suction). (7) Finally, **the osmotic pressure** (or suction) **exercised by a certain quantity of a substance in dilute solution is identical in value with the gaseous pressure which the same quantity of the same substance would exercise if it were contained as a gas in the same volume at the same temperature.** Thus 44 g. of carbon dioxide, as a gas, filling 22.4 liters (the G.M.V.) at 0° exercises one atmosphere gaseous pressure. When the cube is filled with water, and the gas is thus dissolved, the osmotic pressure of the solution is one atmosphere.

These facts apply to substances which are not acids, bases, or salts. We shall find later (see Chap. XVI) that the osmotic pressures of the members of these three classes of substances are frequently abnormally high, but that the abnormality is easily explained.

Osmotic pressure (or suction) is a subject of great interest in connection with the physiology of plants and animals. It aids in explaining why a withered flower, containing a *solution* in its cells, revives when placed in pure water. The latter enters through the walls of the cells, and the pressure thus produced distends the structure and stiffens it. Similarly, the ascent of the water from the soil into the roots and through the stem of a growing plant is explained. In the animal body also, osmosis plays a large part.

Measurements of osmotic pressures cannot be made accurately with a diffusion shell, because the solute is able to some extent to pass through the material. Then, too, such a shell can be used only with dilute solutions, because it will not withstand high pressures. In making accurate measurements, a cell of porous porcelain is used, and the pores are filled with a gelatinous precipitate of cupric ferrocyanide $Cu_2Fe(CN)_6$ (*q.v.*).

Densities of Solutions. — The density or specific gravity of a solution is usually greater than that of water and, in each case, varies with the concentration. For commercial purposes, the concentrations of solutions are commonly defined by the specific gravity. Thus, we purchase ammonium hydroxide solution of "0.88 sp. gr.," meaning 35 per cent of ammonia, or sulphuric acid of "1.84 sp. gr.," meaning 94.8 per cent of the acid.

The commonly greater density of a solution is utilized in making solutions in chemical factories. Shaking several tons of the mixture is out of the question, and stirring costs money. If the solid is placed in the bottom of the tank, under water, a saturated solution is formed in the lowest layer of the water, and passage of the dissolving substance into the upper layers, by diffusion, would take months or years. Hence most of the solid would remain undissolved (Fig. 57, p. 127). But when the solid is placed on a *shelf* near the surface of the water, the solution sinks through the water, fresh water rises to the shelf, and a circulation is started. This results in the dissolving of the whole material in a surprisingly short time, with no expenditure of labor whatever.

Changes in Volume upon Solution. — The erratic and, at present, unexplained changes in volume which occur when a substance is dissolved, seem to indicate that the process is less simple than we have thus far admitted, and that chemical changes occur during the process. Thus, when 250 g. of common salt are dissolved in 1 liter of water (= 1000 c.c. = 1000 g.), which gives a 20 per cent solution, the volume of the solution is only 1086 c.c. Since the 250 g. of salt occupied 116 c.c. before being dissolved, a *shrinkage* of 1116 − 1086 or 30 c.c. accompanied the process of solution. On the other hand, 214 g. of ammonium chloride (volume 142.5 c.c.) and 843.5 c.c. of water, have a total volume of 986 c.c., but when dissolved give 1000 c.c. of solution. Here there is an expansion of 14 c.c. Table sugar, however, dissolves in water with almost no change in volume.

Is Solution a Physical or a Chemical Change? — These phenomena are, in part, accounted for by the fact that water is not a single substance, but a mixture. It is largely composed of dihydrol $(H_2O)_2$, with much trihydrol $(H_2O)_3$ near to 0° and increasing quantities of monohydrol H_2O at higher temperatures.

When *any* substance is dissolved in considerable amount in water, the equilibrium amongst these three kinds of molecules is disturbed, and their proportions change:

$$2(H_2O)_3 \leftrightarrows 3(H_2O)_2 \leftrightarrows 6H_2O.$$

Now, equal weights of these three kinds of water occupy different volumes, and hence solution is accompanied by changes in the volume of the *water*. The same condition in water explains the point of maximum density (4°). The change from $(H_2O)_3$ to $(H_2O)_2$, which proceeds as the temperature rises from 0° to 4°, is accompanied by a *shrinkage*, because dihydrol has the higher density. Beyond 4°, the usual expansion with rising temperature prevails.

There is also evidence that many dissolved bodies form unstable compounds with water, although we have not as yet definite information about these compounds.

Dissolving in water is, therefore, partly a chemical and only partly a physical process — a part of the water is always affected, and a part or all of the solute may go into combination.

Exercises. — 1. Give other examples of limited solubility in various solvents (p. 122).

2. What weights of phosphoric acid (p. 94) and of sodium hydroxide, respectively, are required to make 1 liter of a normal solution?

3. Express the concentrations of solutions of ammonium chloride, saturated at 0° (sp. gr. 1.076), and of potassium sulphate K_2SO_4, saturated at 10° (sp. gr. 1.083), in terms of a normal solution (p. 124).

4. Express the concentration of a five per cent aqueous solution of phosphoric acid (sp. gr. 1.027), in terms of a normal and a molar solution, respectively.

5. Explain why, (*a*) pulverization and, (*b*) agitation hasten the dissolving of a solid (*cf.* pp. 331, 398).

6. Read from the curves (p. 131) the solubilities of potassium nitrate at 15°, of potassium chloride at 30°, of potassium chlorate at 45°. What are the relative rates at which the solubilities of these salts increase with rise in temperature?

7. If 5 g. of a substance, dissolved in 1000 c.c. of water, give a

solution freezing at −0.2°, what is the molecular weight of the substance?

8. At what point in a tank of water should you introduce ammonia gas, in order, with the least effort, to saturate the water? The sp. gr. of the saturated solution is 0.88.

9. 6 grams of a substance when dissolved in 200 c.c. of water give a boiling-point of 102.6°. What is the molecular weight of the substance?

10. 1.6 grams of naphthalene $C_{10}H_8$ when dissolved in 25 g. of benzene (freezing-point 5.48°) gives a solution which freezes at 3.03°. When 2.44 grams of another substance are dissolved in the same amount of benzene, the solution freezes at 3.52°. What is the molecular weight of the latter substance?

11. The elevation of the boiling-point in the above solution of naphthalene is 1.285°. What elevation of the boiling-point is produced in the second solution?

CHAPTER XI

HYDROGEN CHLORIDE. CALCULATIONS

We have had occasion several times to mention common salt, or sodium chloride NaCl. This is one of the most familiar chemical substances. Large quantities of it are used in the household, in cooking and in making freezing mixtures. Still larger amounts are consumed in manufacturing washing soda, caustic soda, and soap, for all of which it furnishes the necessary sodium. It is used also in preserving fish and other foods. It supplies the chlorine used in bleaching and in the sterilization of city waters. We shall consider it first as a means of making other compounds of chlorine.

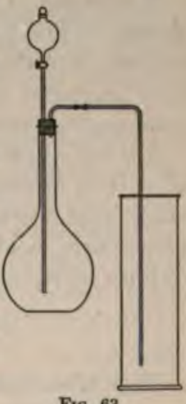

Fig. 63.

Preparation of Hydrogen Chloride HCl from Salt. — When some concentrated sulphuric acid is poured upon sodium chloride, a vigorous effervescence is noticed. This shows that bubbles of a gas are forming upon the salt crystals and are rising through the acid and bursting. If the salt be placed in a flask (Fig. 63), the acid can be allowed to enter from time to time through the funnel. When the air has been displaced from the flask, the gas issues from the delivery tube. If the correct proportion of the acid is used, and only a gentle heat is applied, all that remains in the flask is a white solid, sodium-hydrogen sulphate (sodium bisulphate) $NaHSO_4$:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow .^* \qquad (1)$$

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* The arrow directed downwards indicates elimination of a substance by precipitation; that directed upwards, escape as a gas or solution of a solid.

The gas is extremely soluble in water and, being heavier than air, may be collected by upward displacement of the air in a jar.

The action described is the one which occurs in the laboratory. When a double proportion of salt and a high temperature are used, a second action occurs:

$$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl \uparrow$$

and sodium sulphate Na_2SO_4 remains. In Europe this action is employed, with furnace heat, in manufacturing sodium sulphate, from which sodium carbonate is afterwards prepared. The hydrogen chloride passes into a tower, down which water trickles over lumps of coke, and is dissolved. The aqueous solution is called hydrochloric acid or, in commerce, muriatic acid (Lat., *brine acid*).

Hydrogen Chloride from Other Chlorides and Other Acids. — The chlorides of other metals could be substituted for sodium chloride in this action, and all the more soluble ones would give hydrogen chloride freely. Other chlorides are all more expensive, however, than is common salt.

All acids contain the necessary hydrogen radical, and might offer it in exchange for the sodium in the salt, yet in practice no other acid works so well as does sulphuric acid. Concentrated phosphoric acid H_3PO_4,Aq acts more slowly, giving primary sodium phosphate:

$$NaCl + H_3PO_4 \rightarrow NaH_2PO_4 + HCl \uparrow.$$

The Molecular View of the Interaction of Sulphuric Acid and Salt. — One who has used the above-described methods for making hydrogen chloride without reflection would not realize the complexity of the machinery by which the result is achieved. The means are apparently very simple. Yet the mechanical features of this experiment, when laid bare, are extremely curious and interesting. A single fact will show the possibilities which are concealed in it.

If we take a saturated solution of sodium-hydrogen sulphate in water and add to it a concentrated solution of hydrogen chloride in water (concentrated hydrochloric acid), we shall perceive at once the formation of a copious precipitate. This is composed entirely of minute cubes of sodium chloride:

$$NaHSO_4 + H\text{[illegible]}\rightarrow H_2SO_4 + NaCl\downarrow.^* \qquad (2)$$

Now this action is nothing less than the precise reverse of (1), yet it proceeds with equal success. In fact, this chemical interaction is not only reversible (pp. 93, 95), but can be carried to completion in *either* direction. It is only in presence of a large amount of water that it stops midway in its career and is valueless for securing a complete transformation in either direction:

$$NaHSO_4 + HCl \rightleftarrows H_2SO_4 + NaCl.$$

In an action which is reversible, if the *products* remain as perfectly mixed and accessible to each other as were the initial substances, their interaction will continually undo a part of the work of the forward direction of the change. Hence, in such a case the reaction must, and does, come to a standstill while as yet only partly accomplished; but this was not the case with actions (1) and (2). Let us examine the means by which the premature cessation of each was avoided.

In equation (1) the salt dissolved to some extent in the sulphuric acid, $NaCl$ (solid) $\rightleftarrows$ $NaCl$ (dslvd), and so, by contact of the two kinds of *molecules*, the products were formed. On the other hand, the hydrogen chloride, being insoluble in sulphuric acid, escaped as fast as it was formed: HCl (dslvd) $\rightleftarrows$ HCl (gas). Hence, in that case, almost no reverse action was possible, and the double decomposition went on to completion. With all the sodium-hydrogen sulphate in the bottom of the flask, and most of the hydrogen chloride in the space above, the two products might as well have been in separate vessels so far as any efficient re-interaction was concerned. This plan, in which water is purposely excluded, forms therefore the method of making hydrogen chloride.

In equation (2), on the other hand, the hydrogen chloride was taken *in aqueous solution*, and was mixed with a strong solution of sodium bisulphate. The acid was, therefore, kept permanently in full contact with the sodium bisulphate. It had in this case, every opportunity to interact with the latter and no chance of escape. Every molecule of each ingredient could reach every molecule of the other with equal ease. Furthermore, the sodium chloride, produced as a result of their activity, is not very soluble in concentrated hydrochloric acid (far less so than in water), and so it came out as a precipitate: NaCl (dslvd) ⇄ NaCl (solid). But this was almost the same as if it had gone off as a gas. It meant that the greater part of the salt was in the solid form. It was in a state of fine powder, it is true. But, in the molecular point of view, the smallest particle of a powder contains millions of molecules, and most of these are necessarily buried in the interior of a particle. Thus, the sodium chloride was no longer able to interact effectively molecule to molecule with the other product, the sulphuric acid. Hence, there was little reverse action to impede the progress of the primary one. Thus (2) is nearly as perfect a way of liberating sulphuric acid as (1) is of liberating hydrogen chloride.

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* See footnote to p. 141.

This discussion is given to illustrate the displacement of a chemical equilibrium, and to explain the method of preparing hydrogen chloride. It also throws an interesting light on **chemical affinity**, however. Considering action (1), by itself, we might reason that the hydrogen chloride was formed because the affinity of the hydrogen (H) for chlorine (Cl) was greater than for the sulphate radical (SO_4). But, if we did so, then in action (2) we should be compelled to reason similarly that the preponderance of affinity was just the opposite. In point of fact, no conclusion about relative affinity can be drawn from these actions. The effects of affinity are here entirely subordinated by the effects of a purely mechanical arrangement, depending on solubility. When the activities of the acids are properly compared, hydrochloric acid is found to be considerably more active than sulphuric acid.

Physical Properties. — Hydrogen chloride is a colorless gas, which produces a suffocating effect when inhaled.

Density (H = 1), 18.23.
Weight of 22.4 l., 36.73 g.
Sol'ty in Aq (0°), 50,300 vols. in 100.
Crit. temp., +52°.
Boiling-point (liq.), −83.7°.
Melting-point (solid), −110°.

The gas is one-fourth heavier than air. On account of its great solubility, when it streams into the air it condenses atmospheric moisture into a fog (of drops of hydrochloric acid). The extreme solubility may be shown by filling a dry flask (Fig. 64) with the gas. The "dropper" contains water, and is closed at the tip with soft wax. A drop of water, expelled by pinching the "dropper," dissolves so much of the gas that the water is forced in by atmospheric pressure, like a fountain, through the longer tube.

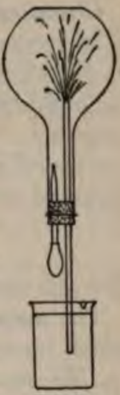

FIG. 64.

Both in the gaseous and liquefied states it is a non-conductor of electricity. Its heat of solution is 17,400 calories (p. 85). On account of its high concentration, the saturated, aqueous solution may be looked upon as a mixture of liquefied hydrogen chloride and water.

When the *concentrated* aqueous solution is heated, it is the gas and not the water which is driven out, for the most part. When the concentration has been reduced to 20.2 per cent, the rest of the mixture distils unchanged at 110°. This occurs because, at this concentration, the gas is carried off in the bubbles of steam in the same proportion in which it is present in the liquid. If a *dilute* solution is used, *water* is the chief product of distillation (about 100°), but gradually the boiling-point rises and, when the concentration has reached 20.2 per cent once more, the same hydrochloric acid of **constant boiling-point** (110° at 760 mm.), as it is called, forms the residue.

Chemical Properties. — Hydrogen chloride is extremely stable, as we might expect from the vigor with which the elements of which it is composed combine (see p. 160). On being heated to a temperature of 1800°, however, it begins to dissociate into its constituents.

In the chemical point of view, it is on the whole rather an indifferent substance. Hydrogen chloride (the gas) has no action upon any of the non-metals, such as phosphorus, carbon, sulphur, etc. Many of the metals, however, particularly the more active ones, such as potassium, sodium, and magnesium, decompose it. Hydrogen is set free, and the chloride of the metal is formed. The equation representing the weights is $K + HCl \rightarrow KCl + H$. But the molecular formula (p. 111) of hydrogen is H_2, hence the correct equation is:

$$2K + 2HCl \rightarrow 2KCl + H_2.$$

Hydrogen chloride unites directly with ammonia gas to form a cloud of solid particles of ammonium chloride ($HCl + NH_3 \rightarrow NH_4Cl$).

Chemical Properties of Hydrochloric Acid. — The solution of hydrogen chloride in water is an entirely different substance in its chemical behavior from hydrogen chloride. It **is strongly acid,** turning blue litmus red. The gas and liquefied gas have no such property. The solution **conducts electricity** very well, and is decomposed in the process (p. 55), giving hydrogen at the negative wire and chlorine at the positive wire:

$$2HCl \rightarrow H_2 \text{ (neg. wire)} + Cl_2 \text{ (pos. wire)}.$$

The gas and the liquefied gas are practically nonconductors.

The **metals** preceding hydrogen in the order of activity (p. 60), when introduced into hydrochloric acid, **displace the hydrogen** (p. 55), and form the chloride of the metal. In the case of zinc the action was represented by the equation:

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2.$$

The aqueous solution of hydrogen chloride **interacts** rapidly **with** most **oxides and hydroxides of metals,** as, for example, those of zinc:

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O,$$
$$Zn(OH)_2 + 2HCl \rightarrow ZnCl_2 + 2H_2O.$$

Here no free hydrogen is obtained, since the oxygen in the oxide, and the hydroxyl in the hydroxide, unite with it to form water. In each case, however, the chloride of the metal is obtained. It may be noted, in passing, that all acids behave in a similar manner towards oxides and hydroxides of metals, giving water and a compound corresponding to the chloride. Dilute sulphuric acid, for example, gives sulphates.

Modes of Preparing Chlorides. — In the preceding section three kinds of actions, each constituting a different **mode** of **preparing chlorides,** have been mentioned incidentally. There are two others. The simplest is the direct union of the element with chlorine ($Zn + Cl_2 \rightarrow ZnCl_2$). The other method is illustrated in the case of the precipitation of silver chloride by adding a solution of a chloride to a solution of silver nitrate. Here the formation of the chloride occurs by exchange of another radical (p. 53) for the chloride radical:

$$AgNO_3 + NaCl \rightarrow AgCl \downarrow + NaNO_3.$$

The insoluble chlorides (see p. 164) can be made conveniently by this plan. The formation of the precipitates, for example that of silver chloride, is used as a **test** for the presence of a soluble chloride in the solution.

Uses of Hydrochloric Acid. — This substance is used, in Europe, as a commercial source of chlorine. It is employed in cleaning metals, and in the manufacture of chlorides of metals. It is an important component of the gastric juice of the stomach, although the proportion is only about 1 part in 500.

Precipitation. — When two soluble substances are dissolved, separately, and the solutions are mixed, chemical interaction frequently occurs, as in the case of salt and silver nitrate (see also p. 143). If one of the products is insoluble, then a supersaturated solution of this product is at once produced. As a rule, this substance almost immediately becomes visible as a fine powder, called a **precipitate,** suspended in the liquid.

The insoluble product can often be recognized by its physical appearance, and so this sort of action is frequently used as a test for one of the *original* substances. Thus many precipitates have a distinctive **color.** Again, precipitates which are colorless, or have the same color, differ in appearance, and are described as **gelatinous, curdy, pulverulent,** or **crystalline.** In the first two cases, the precipitation is so sudden that there is no time for crystals to be formed, and the product is **amorphous** (Gk., *without form*). Thus silver chloride is curdy, and precipitated sodium chloride (p. 143) is crystalline.

Fourth Variety of Chemical Change: Double Decomposition. — In this chapter we encounter for the first time the fourth variety of chemical change. Upon examining the equation for the action of sodium chloride and silver nitrate, we see that the silver nitrate decomposed into its radicals (Ag) and (NO_3).

The sodium chloride also decomposed into its radicals (Na) and (Cl). The (Ag) then united with the (Cl) and the (Na) with the (NO_3).

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3.$$

Since both of the original substances decomposed, this is called a **double decomposition.** An exchange of radicals occurred.

The action by which hydrogen chloride was prepared (p. 142) belonged to the same class:

$$NaCl + HHSO_4 \rightarrow NaHSO_4 + HCl.$$

Double decompositions involving acids, bases, and salts are all reversible reactions. The fact that many of them proceed, nevertheless, to practical completion has already been explained at length (pp. 142–144).

The Varieties of Chemical Change. — Most chemical changes belong to one of the four varieties:

1. Combination, *e.g.*, $Fe + S \rightarrow FeS$.
2. Decomposition, *e.g.*, $2KClO_3 \rightarrow 2KCl + 3O_2$.
3. Displacement, *e.g.*, $Zn + 2HCl \rightarrow H_2 + ZnCl_2$.
4. Double Decomposition, *e.g.*, $AgNO_3 + HCl \rightarrow AgCl + HNO_3$.

In the first, 2 (or more) substances give 1 substance.

In the second, 1 substance gives 2 (or more) substances.

In the third, 1 element and 1 compound give 1 element and 1 compound.

In the fourth, 2 compounds give 2 compounds.

Occasionally, one compound gives one (different) compound, a change called **internal rearrangement.** Nearly all chemical changes, so far as their *mechanism* is concerned, can be classified under one or other of these five kinds.

A **dissociation** (p. 93) is *both* a combination and a decomposition, because it is reversible. For example:

$$2H_2O \rightleftarrows 2H_2 + O_2.$$

Electrolysis is decomposition by an electric current.

The foregoing varieties of chemical action are general, and not limited to any classes of elements. **Oxidation** (p. 36) and **reduction** (p. 37) are so limited. Thus combination with oxygen is oxidation, while combination with hydrogen is reduction. A more complete discussion of action of these classes will be given later (see Chapter XXIII).

The reader should classify each action mentioned in the text, and so become familiar with the chemical point of view which this classification represents.

Salts. — We have seen that an acid contains hydrogen H as a radical (p. 52), and a base contains the radical hydroxyl OH (p. 94). The name **salts** is given to the class of substances which contain a positive and a negative radical, **neither of which is hydrogen nor hydroxyl.** For example, NaCl, Na_2SO_4, $AgNO_3$ are the formulæ of salts. Salts are so named because they resemble common salt in having two radicals, and entering readily into double decomposition.

Sodium-hydrogen sulphate $NaHSO_4$ is classed as an **acid salt,** because it has a positive and a negative radical, and a hydrogen radical in addition.

CALCULATIONS

Familiarity with the interpretation of **molecular equations** is best obtained by making simple calculations based upon their common uses in chemistry.

Weights. — When a problem in regard to **weights** of material used or produced in a given action is to be solved, the molecular equation is to be written and the weights inserted beneath the formulæ. The mode of calculation has been described already (pp. 67, 116).

Weights and Volumes. — When a problem involving **weights and volumes** is to be solved, the molecular equation is to be written, and both the weights and volumes are to be inserted. Note, however, that only the volumes of the substances *in the gaseous condition* are considered.

For example, what volume of oxygen is obtained from 60 g. of potassium chlorate? The molecular equation, made as already described (p. 116), together with the full interpretation, are as follows:

$$\begin{array}{lccccc} & 2KClO_3 & \rightarrow & 2KCl & + & 3O_2. \\ \textsc{Weights}: \left\{ \right. & \underbrace{2\,(39.1+35.46+48)}_{245.1\text{ g.}} & & \underbrace{2\,(39.1+35.46)}_{149.1\text{ g.}} & & \underbrace{3\times 32}_{96\text{ g.}} \\ \textsc{Volumes}: & & & & & 3\times 22.4\text{ l.} \end{array}$$

Observe that no volumes are given under the chlorate and chloride of potassium. This is because their volumes in the *gaseous* condition can be of no practical use, since they are solids which are melted, *but not vaporized* during this, or any action in which we employ them. Now, as to the problem in hand, it is concerned with a weight of potassium chlorate and a volume of oxygen. Reading from the equation, our information on *these* points is that 245.1 g. of potassium chlorate give 67.2 liters (observe that the *coefficients* are used, as well as the molecular weights, in these numbers) of oxygen at 0° and 760 mm., and the question is: What volume will 60 g. give? By proportion, 245.1 g.: 67.2 l. :: 60 g.: x l., where $x = 16.45$ liters. If a different temperature and pressure had been specified, either the volume in the equation, or the answer, would have had to be converted, by rule, to the given conditions.

It saves time not to write out, as above, the whole interpretation, but only the parts required. For example, if the question is: What volume of chlorine is needed to give 25 g. of aluminium chloride? we may, if we choose, omit all the data excepting the volume of the chlorine and the weight of the aluminium chloride, thus:

$$\begin{array}{ccccc} 2Al\ + & 3Cl_2 & \rightarrow & 2AlCl_3 \\ & 3\times 22.4\text{ l.} & & 2\times 133.5\text{ g.} \end{array}$$

The volume of chlorine required is $25 \times 3 \times 22.4 \div (2 \times 133.5)$ liters. These illustrations show the method of calculating actual volumes (see Exercises 1, 2).

Relative Volumes Alone. — If the question concerns **relative volumes** only, then it is simplest to use the interpretation of the equation in terms of molecules. For example: What relative volumes of hydrogen chloride and oxygen are required in Deacon's process (see p. 155)? The molecular equation is

$$\begin{array}{lccccccc} & 4HCl & + & O_2 & \rightarrow & 2H_2O & + & 2Cl_2. \\ \textsc{Molecules}: & 4 & & 1 & & 2 & & 2 \end{array}$$

Since equal numbers of molecules of gases occupy equal volumes, the proportion 4 molecules of hydrogen chloride to 1 molecule of oxygen shows the ratio to be 4 : 1 by volume. Similarly, every 4 molecules of hydrogen chloride give 2 molecules of chlorine, so that the ratio of these substances by volume is 4: 2, or 2 : 1.

In regard to the water, since that is not a gas at common temperatures, the question, if asked, must be more specific: What are the relative volumes of *steam* and chlorine in the product, as commonly delivered by this action at 400°? It is 2 : 2, or 1 : 1. What are the relative volumes of water and chlorine, after the products have cooled to room temperature? The water is no longer a gas, so that it occupies, relatively, almost no volume.*

What is the total volume-change in the foregoing action above 100°? It is a change from 5 molecules to 4. The volume changes in the same ratio. But at 0° the volume-change is from 5 volumes to 2, for the water does not appreciably add to the volume of the products (see Exercises 3, 4).

Relative Volumes, Again. — When we know the molecular formulæ of the single substances concerned in an action, the equation can be made, and **the relative volumes determined, without actual measurement.** For example: What volume-change will be observed when a mixture of carbon monoxide and oxygen has exploded, and the temperature has once more reached that of the room? The molecular formulæ are CO, O_2, and CO_2. The equation representing the weights is $CO + O \rightarrow CO_2$. The molecule of oxygen, however, being O_2, we cannot employ less than this quantity in a molecular equation, so that the equation becomes:

$$2CO + O_2 \rightarrow 2CO_2.$$

Three molecules, therefore, give two, throughout the whole mass, and therefore three volumes will become two, if the pressure and temperature are the same at the beginning and end of the action.

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* Of course if an exact answer *must* be given, it can be given. But for this we require the weight and specific gravity of the product. Thus, $2H_2O$ represents 2 × 18 g. of water. The sp. gr. of water is 1. Therefore the volume of water formed is 36 c.c. The volume of $2Cl_2$ is 2 × 22.4, or 44.8 liters at 0°. The ratio of water to chlorine by volume at 0° is therefore 36: 44,800. But, as a rule, we simply give the volumes of solids and liquids as *zero*, compared with those of the gases concerned in the same action.

If we remember that all volatile compounds of carbon and hydrogen burn to form water and carbon dioxide, the molecular equation for any such combustion may easily be made, and the volumes of all the materials ascertained. When water is a product, only its volume as steam is given by the equation (see Exercises 4, 5).

Relative Densities of Gases. — Knowing by heart the molecular formulæ of gaseous substances, as we must know them for many purposes, it is unnecessary to burden our minds with other data in regard to **the relative weights of gases.** Is hydrogen chloride (HCl) heavier or lighter than carbon dioxide (CO_2)? These formulæ represent the weights of equal volumes (22.4 l.), namely, 36.46 g. and 44 g., respectively. Hence the former gas is a little lighter.

Remembering that the G.M.V. of **air** weighs 28.955 g. (Table, p. 101), we can compare the weight of any gas with that of air in the same way. What are the relative weights of acetylene (C_2H_2, p. 105) and sulphur dioxide (SO_2) as compared with air? The G.M.V. cube holds formula-weights of the first two, namely 26 g. and 64 g., and 28.955 g. of air. Hence acetylene is a little lighter than air, and sulphur dioxide more than twice as heavy (see Exercise 6).

Exercises. — 1. What volume of oxygen at 10° and 750 mm. is obtainable by heating 50 g. of potassium chlorate (pp. 116, 150)?

2. What volume of oxygen at 20° and 760 mm. is required to convert 16 g. of iron into dehydrated rust (Fe_2O_3) (p. 150)?

3. Write out the molecular equations for the interactions of methane and chlorine giving CH_3Cl; and for the burning of phosphorus (vapor) in oxygen (p. 105). Deduce the volume relations of the initial substances, and of the products, at various temperatures in each case.

4. Write out the molecular equations for the interactions of acetylene and oxygen (p. 105), and of alcohol vapor (b.-p. 78°) and oxygen. Deduce the volume relations of the initial substances and of the products at 0° and at 100° in each case.

5. The molecular weight of cyanogen is 52.08. What is its density referred to air, and what the weight of 1 l. at 0° and 760 mm.? It contains 46.08 per cent carbon and 53.92 per cent nitrogen.

What is the formula of the substance (p. 45)? Exploded with oxygen it forms carbon dioxide and free nitrogen. What will be the relative volumes of the materials before and after the interaction (p. 151?)

6. What are the relative weights of equal volumes of hydrogen sulphide (H_2S), and hydrogen iodide (HI), compared with air (p. 152)?

CHAPTER XII

CHLORINE

Chlorine was first recognized as a distinct substance by Scheele (1774). He obtained it from salt by means of manganese dioxide, using the method described below. It was supposed to be a compound containing oxygen until Davy (1809–1818) demonstrated that it was an element.

Occurrence. — Chlorine does not occur free in nature. There are, however, many compounds of it to be found in the mineral kingdom. Sea-water contains a number of chlorides in solution. Of the 3.6 per cent of solid matter in sea-water, nearly 2.8% is sodium chloride $NaCl$. During past geological ages the evaporation of sea-water has led to the formation of immense deposits of the compounds usually found in such water. Thus, at Stassfurt, such strata attain a thickness of over a thousand feet. Certain layers of these strata are composed mainly of sodium chloride (rock salt). In other layers potassium chloride (sylvite), an indispensable fertilizer, and other compounds of chlorine, occur.

Preparation. — Chlorine cannot be obtained with the same ease as oxygen. There are only a few chlorides, such as those of gold and platinum, which lose chlorine when heated, and they are too expensive or difficult to make for laboratory use. We employ therefore methods like those used for the preparation of hydrogen (*cf.* p. 53). We may (1) decompose any chloride by means of electricity, just as, to get hydrogen, we electrolyzed a dilute acid (p. 55). Or (2) we may take some inexpensive compound of chlorine, such as hydrogen chloride (HCl), and by means of some simple substance which is capable of uniting with the other constituent — here oxygen serves the purpose — secure the liberation of the element. Or (3) — and this turns out to be the most convenient laboratory method — we may use a more complex action.

Electrolysis of Chlorides. — Hydrogen chloride and those chlorides of metals which are soluble in water are all decomposed when a current of electricity is passed through the aqueous solution. They yield chlorine at the positive electrode. The other constituent, the hydrogen (Fig. 65), manganese, or whatever it may be, is liberated at the negative wire. Since the chlorine is soluble in water, the effervescence due to its release is not noticeable until the liquid round the electrode has become saturated with the gas: Cl_2 (dslvd) $\rightleftarrows$ Cl_2 (gas). The shape of the apparatus keeps the two products from mingling. The presence of the chlorine in the liquid at the positive end may be shown by a suitable test (p. 161).

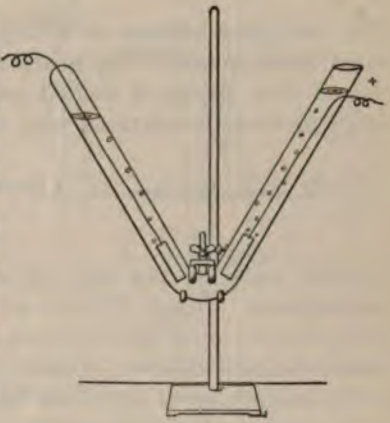


Fig. 65.

In commerce chlorine is now obtained chiefly by this method, sodium chloride or potassium chloride being the source of the element. Electrodes of artificial graphite are used, as most other conductors unite with the chlorine. The potassium or sodium, as the case may be, travels towards the negative electrode, but is not liberated. Instead, potassium or sodium hydroxide (*q.v.*) accumulates in the solution round the plate and hydrogen escapes. The chlorine is released at the positive electrode, as usual. The hydrogen, the hydroxide and the chlorine all find commercial applications. The chlorine is either liquefied by compression in steel cylinders or is employed at once for making bleaching powder (see index).

Action of Free Oxygen on Chlorides. — Sodium chloride is the cheapest source of chlorine, but oxygen does not interact with it even at a high temperature. By treating the sodium chloride with sulphuric acid, therefore, the chlorine is first transferred into combination with the hydrogen of the acid, giving hydrogen chloride (p. 141). In order to liberate chlorine from the hydrogen chloride, we may then combine the hydrogen with oxygen obtained from the air.

Skeleton: $HCl + O \rightleftarrows H_2O + Cl.$
Balanced: $2HCl + O \rightleftarrows H_2O + 2Cl.$
Molecular: $4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2.$

The two gases interact so slowly, however, that a contact agent must be employed. The mixture of air and hydrogen chloride is passed over pieces of heated pumice-stone (Fig. 66) or broken brick previously saturated with cupric chloride solution. A temperature of about 370° is used. Furthermore, the action is reversible (read the equation backwards) and equilibrium is reached when 80 per cent of the hydrogen chloride has been decomposed. Hence 20 per cent of this gas passes on unchanged. Only 80 per cent of the hydrogen chloride and oxygen are changed into steam and chlorine, because the latter substances are continuously interacting to reproduce hydrogen chloride and oxygen. If one substance could be separated (p. 143) from the other, to prevent the backward action, the yield would be raised to 100 per cent. In the product, the chlorine is mixed with steam and with a very large volume of nitrogen which entered with the oxygen, as well as with unused hydrogen chloride, so that, for making the pure substance, this method (**Deacon's process**) is quite unsuitable. Bleaching powder, however, can be made by its means.

FIG. 66.

The relative volumes in this reaction (see p. 150) are indicated by the numbers of molecules in the equation. Four volumes of hydrogen chloride and one volume of oxygen give two volumes of steam and two volumes of chlorine.

The above action is spoken of as an oxidation. It is true that no oxygen is actually introduced into the hydrogen chloride as a whole. The removal of hydrogen from combination with the chlorine is, however, the first step towards the introduction of oxygen into combination with the latter, and is essentially an oxidation.

Action of Combined Oxygen upon Chlorides. — The best laboratory method for making chlorine is to place some solid potassium permanganate in a flask, arranged like that in Fig. 67. Concentrated hydrochloric acid (an aqueous solution of hydrogen chloride), diluted with one-third of its volume of water, is allowed to fall upon the compound drop by drop from the dropping funnel. The action is very rapid, the acid is exhausted almost as fast as it falls, and so the stream of gas can be stopped by simply closing the stopcock. The gas is passed through a washing bottle containing water, in order to remove any hydrogen chloride which may be carried over. It may be dried, if necessary, in a second washing bottle containing concentrated sulphuric acid. It cannot be collected over water on account of its solubility, so that jars are usually filled with it by upward displacement of air.

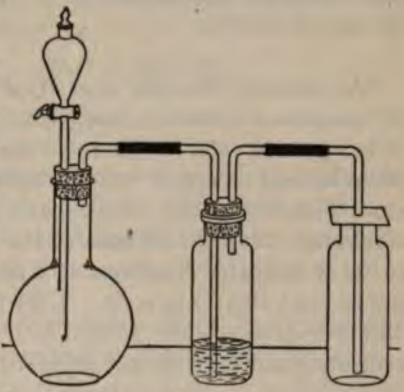


Fig. 67.

Skeleton: $KMnO_4 + HCl \rightarrow H_2O + KCl + MnCl_2 + Cl.$

The O_4, being all converted into water, requires 8H, and therefore 8HCl, for the action. The two metals, potassium and manganese, give their respective chlorides, KCl and $MnCl_2$. This uses 3Cl, and hence 5Cl remains over to be liberated:

Balanced: $KMnO_4 + 8HCl \rightarrow 4H_2O + KCl + MnCl_2 + 5Cl.$
Molecular: $2KMnO_4 + 16HCl \rightarrow 8H_2O + 2KCl + 2MnCl_2 + 5Cl_2.$

The combined oxygen of the permanganate has oxidized the hydrogen chloride, just as did the free oxygen in Deacon's process.

Other Means of Oxidizing Hydrogen Chloride. — Many other compounds of oxygen with metals interact with hydrochloric acid to give free chlorine. Lead dioxide PbO_2, potassium chlorate $KClO_3$, potassium dichromate $K_2Cr_2O_7$, and manganese dioxide MnO_2, are of this nature. The last, being inexpensive, is commonly used in making chlorine. Being an insoluble substance, however, the manganese dioxide acts much more slowly than does the potassium permanganate, which is soluble. A large amount of the materials, and the aid of heat, are required to secure a rapid stream of chlorine.

Manganese Dioxide and Hydrogen Chloride. — The action of manganese dioxide upon hydrochloric acid is an instructive one. It is a **general rule,** of which we shall meet many applications, that **when an acid interacts with an oxide of a metal,** there are two constant features in the result, namely: (1) **The oxygen of the oxide combines with the hydrogen of the acid to form water,** and (2) **the metal of the oxide combines with the acid radical of the acid** according to the valences of each. Here the skeleton equation should be $MnO_2 + HCl \rightarrow H_2O + MnCl_4$. With O_2, to form water, 4HCl is required, and the product is $2H_2O$. Hence the equation is

Balanced: $MnO_2 + 4HCl \rightarrow 2H_2O + MnCl_4$.

This is what happens in the first place. The products actually obtained, however, are water, manganous chloride $MnCl_2$ and chlorine. The manganese tetrachloride can be preserved by cooling the mixture. It is decomposed by the heating, the chlorine escapes, and the other two products remain in the vessel.

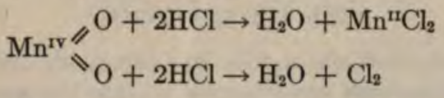
$$MnO_2 + 4HCl \rightarrow 2H_2O + MnCl_2 + Cl_2. \qquad (1)$$

We owe the chlorine to the fact that the tetrachloride is unstable.

If we had used manganous oxide MnO, we should have had a double decomposition:

$$MnO + 2HCl \rightarrow H_2O + MnCl_2, \qquad (2)$$

but we should have got no chlorine. Perhaps the simplest way to describe the difference between these two actions is in terms of the valence of the manganese. In $Mn^{IV}O_2^{II}$ the element is quadrivalent. This means that its atomic weight professes to be able to hold four atomic weights of a univalent element. The four valences of oxygen ($2O^{II}$) can do the same thing. In equation (1) the oxygen fulfils this promise by taking $4H^{I}$. But the Mn^{IV} can hold only $2Cl^{I}$, permanently, and lets the other $2Cl^{I}$ go free. In other words, the *valence* of the atomic weight of *manganese changes* in the course of the action. In equation (2), on the other hand, the manganese is bivalent to start with ($Mn^{II}O^{II}$), and is able to retain the amount of chlorine ($2Cl^{I}$) equivalent to O^{II}. Actions like that of manganese dioxide in (1) are classed as oxidations. The hydrogen chloride, or rather half of it, is oxidized. A graphic mode of writing may make this remark clearer:



$$Mn^{IV}\begin{cases} O + 2HCl \rightarrow H_2O + Mn^{II}Cl_2 \\ O + 2HCl \rightarrow H_2O + Cl_2 \end{cases}$$

The upper half is a double decomposition, the lower an oxidation by half the combined oxygen of the dioxide. The same explanation applies to the interaction of lead dioxide with hydrochloric acid.

Physical Properties. — Chlorine differs from the gases we have encountered so far in having a strong greenish-yellow tint, a fact which gave rise to its name (Gk., *pale green*), and having a powerful, irritating effect upon the membranes of the nose and throat.

Density (H = 1), 35.79.
Weight of 22.4 l., 72.13 g.
Sol'ty in Aq (20°), 215 vols. in 100.
Crit. temp., +146°.
Boiling-point (liq.), −33.6°.
Melting-point (solid), −102°.
Vap. tension (liq.) 0°, 3.66 atmos.
Vap. tension (liq.) 20°, 6.62 atmos.

Since the G.M.V. of air weighs 28.95 g., chlorine is two and a half times heavier. In solubility it stands between slightly soluble gases, like oxygen and hydrogen, and those which are extremely soluble. It can be collected over hot water or a strong solution of salt.

Chlorine was first liquefied by Northmore (1806). It forms a yellow liquid which, contained in steel cylinders lined with lead, is now an article of commerce. On being cooled below −102°, it gives a pale-yellow solid.

In recalling the physical properties of a gas, remember that *six* (p. 31) are required: color, taste, odor, density, solubility, liquefiability.

Chemical Properties. — Chlorine is at least as active a substance as is oxygen. It presents a more varied array of chemical properties than does that element. The binary compounds are called **chlorides.**

Combines with Metals. — Powdered antimony (cold), when thrown into chlorine, unites with it to form the chloride $SbCl_3$, which appears partly as vapor and partly as glowing particles.

Balanced: $Sb + 3Cl \rightarrow SbCl_3$.
Molecular: $2Sb + 3Cl_2 \rightarrow 2SbCl_3$.

Copper, in the condition of thin leaf commonly used for gilding (Dutch-metal), catches fire when thrust into the gas, giving a fog of solid cupric chloride $CuCl_2$. Sodium burns brilliantly, giving a cloud of sodium chloride. The union of a metal like sodium and a colored, irritating gas to give a mild household article, like common salt, illustrates the extraordinary nature of chemical change. All the familiar metals, with the exceptions of gold and platinum, combine readily with chlorine.

When metals (like copper and iron) and chlorine are first thoroughly freed from moisture, combination no longer occurs. A trace of water is required in these, as it is in many other chemical actions, as a contact agent. Hence, the chlorine, before being compressed into steel cylinders, must be freed entirely from water vapor (see Detinning).

Combines with Hydrogen. — A jet of hydrogen burns vigorously in chlorine, producing hydrogen chloride HCl. The union of the gases, when a mixture of them is kept cold and in the dark, is too slow to be perceived. On exposure to diffused light, however, they unite slowly, while a sudden flash of sunlight or the burning of a magnesium ribbon causes instant explosion. The effect of the light is catalytic.

Interacts with Compounds Containing Hydrogen. — When a lighted taper is plunged into chlorine it continues to burn, but a dense cloud of soot (free carbon) rises from the flame. Blowing the breath into the jar then gives the fog which shows the presence of hydrogen chloride. Thus the presence of hydrogen and carbon in the wax is proved. We learn, also, that chlorine has little tendency to combine with carbon, for this element goes free. A few drops of warm turpentine, poured upon a strip of paper, when placed in chlorine give a violent reaction and a cloud of finely divided carbon bursts forth.

$$C_{10}H_{16} + 8Cl_2 \rightarrow 16HCl + 10C.$$

Elements Displaced by Chlorine. — The action on turpentine is a displacement of the carbon by the chlorine. Of the same nature is the action of chlorine upon potassium iodide KI, dry or in solution.

$$2KI + Cl_2 \rightarrow 2KCl + I_2.$$

The iodine, when moist, is deep brown in color. A mere trace of chlorine, liberating a trace of iodine, gives no visible effect. But if some starch is present, even a trace of free iodine yields a deep blue color. This reaction is used as a test for chlorine, for free iodine from any source, and for starch (p. 3). To test for chlorine, strips of filter paper, dipped in starch emulsion (starch boiled with much water and cooled) to which a few drops of potassium iodide have been added, are used. *Combined* iodine, as in potassium iodide, has no effect upon starch. Combined chlorine, as in sodium chloride, has no action upon the prepared strips of paper — free chlorine is required.

Action Upon Water. — We have seen that chlorine seizes the hydrogen in turpentine. We have also learned that it combines with the hydrogen in steam, reversing Deacon's process to the extent of 20 per cent. It also acts upon **cold water,** when dissolved in the latter, although in a similarly incomplete way. The substances formed are hydrochloric acid and **hypochlorous acid** $HClO$:

$$H_2O + Cl_2 \rightleftarrows HCl + HClO.$$

With half-saturated chlorine-water at 10° — that is, water containing an equal volume of chlorine gas — 33 per cent of the chlorine is changed into the acids. Thus, chlorine-water (the solution) is a mixture containing dissolved chlorine and two acids. Hypochlorous acid (*q.v.*) is of especial interest because it is a very active substance, with powerful oxidizing qualities, and bleaches dyes by decomposing them.

The action comes to a standstill when one-third completed, because the two acids interact to reproduce chlorine and water (read the equation backwards). The action is reversible. When the solution is exposed to sunlight, the hypochlorous acid decomposes and oxygen gas is liberated and escapes:

$$2HClO \rightarrow 2HCl + O_2 \uparrow .$$

Since this removes the hypochlorous acid, on whose interaction with the hydrogen chloride the reverse action depends, the forward action *proceeds under continuous illumination* gradually *to completion.* Hence the aqueous solution of chlorine must be kept in the dark, since otherwise, after a time, a dilute solution of hydrogen chloride alone remains.

The reader should note here the displacement of the equilibrium, a chemical one in this case, in consequence of the annulment of one of the opposing tendencies (p. 90). Through the destruction of the hypochlorous acid, one of the tendencies, namely that represented in the backward action, becomes inoperative. The forward action is not itself assisted, but it is no longer impeded, and so proceeds to completion.

Action by Substitution. — When actions like that on turpentine — that is on compounds containing carbon and hydrogen — are moderated by altering the conditions, the decomposition is not so complete. Using a lower temperature is effective. Thus, if methane CH_4 (marsh-gas), the chief component of natural gas, is mixed with chlorine and exposed to sunlight, a slower action occurs, of which the first stage consists in the removal of one unit weight of hydrogen and the **substitution** of chlorine for it according to the following equation:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl.$$

The process may continue further by the substitution* of chlorine for the units of hydrogen one by one until carbon tetrachloride CCl_4 is finally formed.

The action on water is a substitution.

Combines with Non-metals. — Phosphorus burns in chlorine with a rather feeble light, producing primarily phosphorus trichloride PCl_3, a liquid (b.-p. 74°). If excess of chlorine is present, then, as the trichloride cools, it combines to form the solid pentachloride PCl_5. Sulphur, when heated, unites more slowly, giving sulphur monochloride S_2Cl_2, a liquid used in vulcanizing rubber. Chlorine does not combine directly with carbon, nitrogen, or oxygen, although compounds with those elements can be made indirectly. With the helium group of elements (*q.v.*), it forms no compounds.

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* **Substitution** resembles displacement (p. 55) in that an element and a compound interact, and the element takes the place of one unit in the composition of the latter. In the above action, one unit of chlorine takes the place of one unit of hydrogen. But *the latter is not liberated;* it combines with another unit of chlorine. The action resembles double decomposition, excepting that one of the substances is not a compound, but a diatomic element. The name used is intended to fix the attention on the *compound* and on the fact that one unit has been *substituted* for another in it. This conception is a favorite one in the chemistry of compounds of carbon.

Combines with Compounds. — Chlorine unites with many compounds. Thus, one of the oxides of carbon, carbon monoxide CO, when mixed with chlorine and exposed to sunlight gives drops of a volatile liquid (b.-p. 8.2°) known as **phosgene** $COCl_2$.

When chlorine-water is cooled with ice, a compound, chlorine **hydrate** $Cl_2,8H_2O$ crystallizes out. Faraday (1823) placed this substance in the closed limb of a Λ-tube, sealed the open end, and placed the empty limb in cold water (Fig. 68). When the hydrate was gently warmed, chlorine gas was given off and was liquefied by its own pressure in the cold part of the tube.

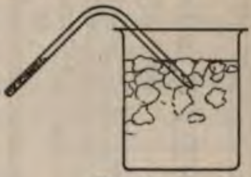

FIG. 68.

Chemical Relations of the Element.* — In the chlorides, an atomic weight of chlorine is equivalent to one atomic weight of hydrogen or of sodium. The element is, therefore, **univalent** (p. 62). It never shows any higher valence than this, save in its oxygen compounds (see Chap. XXIII). The oxides of chlorine interact with water to give acids, and the element is, therefore, to be classed as a **non-metal** (p. 94). It belongs to that **group** of the non-metals called the **halogens**, as a consideration of some others of its relations will show (see Chap. XV).

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* In accordance with the distinction that must be drawn (p. 16) between the element as a variety of matter *in combination*, and the elementary substance or free form of the element, and to avoid a common source of confusion, we shall always give only the behavior of the elementary *substance* under the title *chemical properties*. The characteristics which distinguish the *compounds* of the element, as a class, from, or relate them as a class to the compounds of other elements will then appear in a separate section under the title "Chemical relations" (see pp. 192, 208).

Uses of Chlorine. — Large quantities of chlorine are manufactured for the preparation of bleaching materials and disinfecting agents. In disinfection, the minute germs of disease and putrefaction are acted upon either by the chlorine or by the hypochlorous acid formed by its interaction with water, and instantly their life is destroyed.

Chlorides. — The chlorides are described individually under the other element which each contains. The majority of the chlorides of the metals are easily soluble in water. The chief exceptions are silver chloride AgCl, mercurous chloride (calomel) HgCl, cuprous chloride CuCl, and lead chloride $PbCl_2$. The last of these is on the border line as regards solubility. An appreciable amount dissolves in cold water, and a considerable amount in boiling water (see Table of Solubilities, inside the cover at the front of this book). For the various modes of preparing chlorides see p. 146.

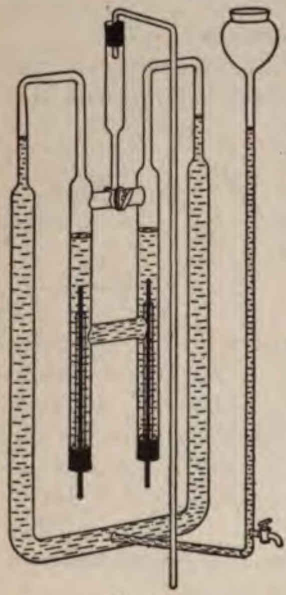

Fig. 69.

Composition of Hydrogen Chloride. — Being now familiar with both hydrogen and chlorine, we may take up the question of the proportion by volume in which the constituents unite, and the relation of this to the volume of the resulting hydrogen chloride.

The decomposition of the solution of hydrogen chloride in water by means of the electric current proves that the gases are liberated in equal volumes. Brownlee's apparatus for demonstrating this is shown in Fig. 69. The central part is the same as in Fig. 27, but, when the three-way stopcock is closed, the gases go to right and left, and displace the liquid in two outside tubes. The equal rate at which this takes place on both sides proves that the gases are generated in equal volumes.

In order to ascertain the relation between the volumes of the constituents and *that of the product*, we may unite the gases and find out whether any change in volume occurs. A tube with thick walls (Fig. 70) is filled with the mixed gases obtained by electrolysis. By dipping one end of the tube under mercury and opening the lower stopcock, it is seen that no gas leaves and no mercury enters. After the mixture has been exploded, by the light from burning magnesium, the same test is repeated with the same result. The pressure has therefore remained equal to that of the atmosphere. Hence there has been no change in volume as the result of the union. It appears, therefore, that

1 vol. hydrogen + 1 vol. chlorine →
2 vols. hydrogen chloride,

a result in harmony with Gay-Lussac's law (p. 98).

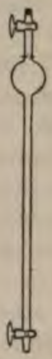

FIG. 70.

Confirmation of the Formulæ Cl_2 and H_2. — According to Avogadro's law, there are equal numbers of molecules in equal volumes of these gases. When hydrogen and chlorine combine, one volume of each of these gases gives two volumes of hydrogen chloride. Let us imagine the experiment to be made with minute volumes holding one hundred molecules each:

$$\overset{\text{HYDROGEN CHLORIDE}}{\boxed{100 \mid 100}} \quad \text{came from} \quad \overset{\text{HYDROGEN}}{\boxed{100}} + \overset{\text{CHLORINE}}{\boxed{100}}$$

The 200 molecules of hydrogen chloride must contain at least 200 fragments of chlorine, since there is a sample in each molecule. Now the 200 fragments of chlorine came from a volume containing only 100 molecules of chlorine. Each of these must therefore have been split in the chemical action. The same is true of each molecule of hydrogen. Hence the molecules of free hydrogen and free chlorine contain at least two atoms. If we consider the molecular formula of a substance as representing one molecule, the equation for this action is:

$$H_2 + Cl_2 \rightarrow 2HCl.$$

There are two molecules on each side of the equation, and this corresponds with the fact that there is no change in the total volume.

Classification of Chemical Interactions and Exercises Thereon. — So far we have defined ten more or less distinct kinds of chemical change, seven differing in mechanism: **Combination** (p. 7), **decomposition** (p. 14), **dissociation** (p. 93), **displacement** (p. 55), **substitution** (p. 162), **double decomposition** (pp. 142, 147), and **internal rearrangement** (p. 148); and three others: **oxidation** (pp. 36, 156, 158), **reduction** (pp. 37, 59), and **electrolysis** (pp. 55, 155). Illustrations of all but one of these will be found in the present chapter. Some actions belong to one of the first seven, and also to one of the three other classes. The ability readily to classify each phenomenon, as it comes up, requires precisely that grasp of the framework of the science which the reader must seek speedily to attain. For example, let him classify the following actions: 1. action of potassium on water; 2. of heat on potassium chlorate; 3. of chlorine on metals; 4. of chlorine on turpentine; 5. of chlorine on potassium iodide; 6. of chlorine on methane; 7. of carbon monoxide and chlorine; 8. of sunlight on hypochlorous acid; 9. of sulphuric acid on salt; 10. of zinc oxide and hydrochloric acid; 11. of zinc on hydrochloric acid.

12. In the interactions of potassium permanganate and of manganese dioxide, respectively, with hydrochloric acid, what fractions of the whole chlorine are liberated? What are the commercial advantages of the use of salt and sulphuric acid with the manganese dioxide?

13. In view of the explanations given, define the general nature of the substances (p. 157) which may be used to oxidize hydrochloric acid.

14. What are the relative volumes of the gaseous interacting substances and products in the following reactions: (*a*) turpentine vapor and chlorine; (*b*) methane and chlorine; (*c*) phosphorus vapor and chlorine; (*d*) carbon monoxide and chlorine.

CHAPTER XIII

ENERGY AND CHEMICAL CHANGE

In describing chemical changes, the fact that heat was evolved has frequently been mentioned. In several instances a current of electricity has been used to produce chemical change. It is now necessary to collect these scattered facts and classify them for future use.

Physical Accompaniments of Chemical Change.—When iron and sulphur combined (p. 13), and when iron burned in oxygen or copper in chlorine, much *heat was developed*. On the other hand, the decomposition of mercuric oxide, as was pointed out (p. 14), owed its continuance to the persistent application of heat and ceased as soon as the source of heat was withdrawn. Here, apparently, *heat was consumed* during the progress of the change, and the chemical action was limited by the amount of heat supplied. The **production or consumption of heat** may, therefore, be a feature of chemical change.

In the burning of iron or magnesium in oxygen, and in the actions of chlorine on copper and turpentine, **light** was also produced. Conversely, silver chloride (p. 147) can be kept any length of time in the dark, but in sunlight it becomes first bluish and then brown, simultaneously giving off chlorine gas and finally leaving only silver as a fine powder. Silver bromide or iodide, in photographic plates, films, and paper, is changed by light in a similar way, liberating the bromine or iodine. It would appear, therefore, that **light may be given out or consumed** in connection with chemical change.

We have seen (p. 155) that a current of **electricity** may be employed to decompose hydrochloric acid and other chlorides, and the battery, or other source of the current must be kept going or the chemical change stops. The inverse of this is likewise familiar. If we place in dilute sulphuric acid a stick of the metal zinc, we find that hydrogen is given off (Fig. 71), that the zinc goes into solution as zinc sulphate (p. 53), and that a large amount of heat is developed. If zinc in fine particles, with much surface, is used, the liquid may even rise spontaneously to the boiling-point. This form of the action produces heat. If, however, we attach the same stick of zinc to a copper wire and, having provided a plate of platinum also connected with a wire, immerse the two simultaneously in the acid (Fig. 72), then a galvanometer, with which the wires are connected, shows at once the passage of a current of electricity round the circuit. Exactly the same chemical change goes on as before. The sole difference is that the gas appears to arise from the surface of the platinum. It is easy to show, however, that the platinum by itself is not acted upon by dilute acids and, in this case, undergoes no change whatever; it serves simply as a suitable conductor for the electricity. Here, then, in place of the heat which the first plan produced, we get an electric current. The arrangement is, in fact, a battery-cell, for a battery is a system in which a chemical action which would otherwise give

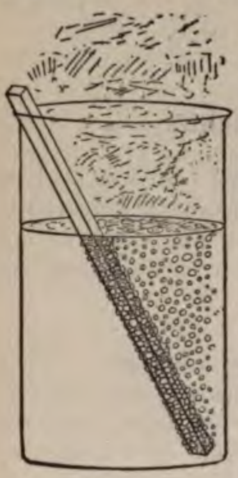

Fig. 71.

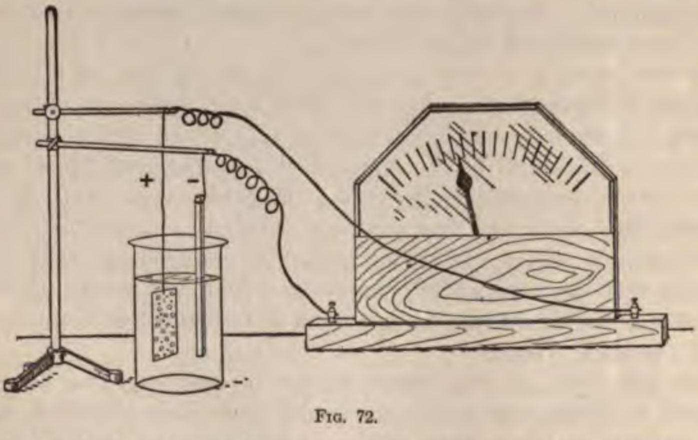

Fig. 72.

heat furnishes electricity instead. Thus, **electrical energy may be consumed or produced** in connection with a change in composition.

Even **violent rubbing** in a mortar, in the case of some substances, can effect an appreciable amount of decomposition in a few minutes. In this way silver chloride can be separated into silver and chlorine, just as by light. It is the **mechanical energy** which is the agent, and part of it is *consumed* in producing the change, and only the balance appears as heat. Conversely, the *production* of mechanical energy, as the result of chemical change, is seen in the behavior of explosives and in the working of our muscles. Thus, **mechanical energy may be used up or produced** in chemical changes.

Summing up our experience, we may state that no change in composition occurs without some accompaniments, such as the production or consumption of heat, light, electrical energy, or, in some cases, mechanical energy.

Classification of the Accompaniments of Change in Composition: Energy. — The problem of classifying (*i.e.*, placing in a suitable category) things like heat, light, and electricity has occupied much attention. In all changes in composition, one of these natural accompaniments is given out or absorbed, sometimes in great amount, yet in none is any alteration in weight observed.* There are many things which are real, however, even if they are not affected by gravitation. In the present instance we reason as follows:

A brick in motion is different from a brick at rest. The former can do some things that the latter cannot. Furthermore, we can easily make a distinction in our minds. The brick can be deprived of the motion and be endowed with it again. Thus, we can get the idea of motion as a separate conception. Similarly, we observe that a piece of iron behaves differently when hot, and when cold, when bearing a current of electricity, and when bearing none. We conceive then of the brick or the iron as having a certain amount and kind of matter which is unalterable, and as having motion, heat, or electricity added to this or removed. Thus, we describe our observations by using two categories, one of which includes the various kinds of **matter**, and the other, various things whose association with matter seems to be invariable and is often so conspicuous. The latter we call the forms of **energy**.

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* Electrons (*q.v.*) do possess mass, but it is very small compared with that of the materials concerned.

The Practical Importance of Energy in Chemistry. — The absorption or liberation of energy accompanying a chemical transformation of matter is often, of the two, the more important feature. We do not burn coal in order to manufacture carbon dioxide gas. We are glad to get rid of the material product through the chimney. It is the heat we want. We do not buy gasoline (petrol) for an automobile in order to obtain various gases to expel through the muffler. We really pay for the mechanical energy. It is the same with burning illuminating-gas or magnesium powder when we want light, and with eating food, which we do, chiefly, to get energy to sustain our activity. We do not run electricity for hours into a storage battery in order to make a particular compound (lead dioxide, for example), but in order to save and store the energy for future use. In industry and life fully half the total amount of chemical change involved is set in motion by us, solely on account of the energy changes it involves. But the production of energy in chemical change is not only thus of practical importance; it is also of scientific interest, as will be seen in the section on energy and chemical activity (see below).

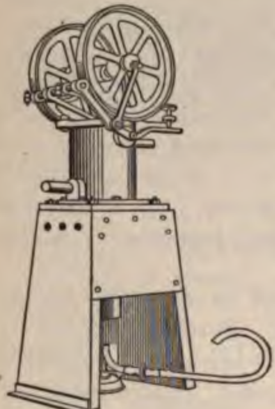

FIG. 73.

Interconvertibility of Forms of Energy: Conservation. — At first sight, these accompaniments of matter seem to be quite unrelated. But a relation between them can be found. If the heat of a Bunsen flame or of the sun is brought under a hot-air motor (Fig. 73) violent motion results. Again, if the motor is connected with a dynamo, electricity may be generated. Still again, if the current from the dynamo flows through an incandescent lamp, heat and light are evolved. Conversely, when motion of the hot-air motor is impeded by a brake, heat appears. When a current of electricity is run through the dynamo, the armature of the latter turns and motion results. But the most significant facts are still to be mentioned. The heat absorbed by the motor is found to be greater when the machine is permitted to move and do work, than when it is not. Thus, it is found that when work is done some heat disappears, and this heat is, in fact, transformed into work. Similarly, when the poles of the dynamo are properly connected and electricity is being produced, and only then, motion is used up. This is shown by the effort required to turn the armature under these circumstances, and the ease with which it is turned when the circuit is open. So, with a conductor like the filament in the lamp, unless it offers resistance to the current and destroys a sufficient amount of electrical energy, it gives out neither light nor heat. Finally, motion gives no heat unless the brake is set, and effort is then demanded to maintain the motion. These experiences lead us to believe that we have here a set of things which are fundamentally of the same kind, for each form can be made from any of the others. We have, therefore, invented the conception of a single thing, of which heat, light, electricity, and motion are forms, and to it we give the name **energy: energy is work and every other thing which can arise from work and be converted into work** (Ostwald).

Closer study shows that equal amounts of electrical or mechanical energy always produce equal amounts of heat. No loss is ever observed in the transformations of energy, any more than in the transformations of matter. Hence, J. R. Mayer (1842), Colding (1843), and Helmholtz (1847) were led independently to the conclusion that **in a limited system no gain or loss of energy is ever observed.** This brief statement of the results of many experiments is called the law of the **conservation of energy.**

Application of the Conception of Energy in Chemistry. — At first sight it looks as if the statement that energy is conserved is not applicable in chemistry. Heat and electricity, for example, seem to be produced and consumed, in connection with changes in composition, in a mysterious manner. We trace light in an incandescent lamp back to the electricity, and this in turn to the mechanical energy, and this again to the heat in the engine. But what form of energy gave the heat developed by the combustion of the coal under the boiler, or by the union of iron and sulphur in our first experiment? Since we do not perceive any electricity, light, heat, or motion, in the original materials, and yet wish to create an harmonious system, we are bound to conceive of the iron and the sulphur, and the coal and the air, as containing another form of energy, which we call **internal energy.** Similarly, when heat is used up in decomposing mercuric oxide, or light in decomposing silver chloride, we regard the energy as passing into, and being stored in the products of decomposition in the form of internal energy.

These conclusions compel us, for the sake of consistency, to think of all our materials as repositories of energy as well as of matter, each of these two constituents being equally real and equally important. A piece of the substance known as "iron" must thus be held to contain so much iron matter and so much internal energy. So ferrous sulphide contains sulphur matter, iron matter, and internal energy. Thus, by a *substance* we mean a distinct species of matter, simple or compound, with its appropriate proportion of internal energy.

In the course of this discussion it has become clear that it is **characteristic** of chemical phenomena that, besides a change in the nature of the *matter*, **there is always an alteration in the amount of internal energy in the system. This alteration involves the production of internal energy from, or the transformation of internal energy into some other form of energy.**

Energy and Chemical Activity. — Other things being equal, actions in which there is a relatively large loss of internal energy proceed rapidly; that is to say, in them a large proportion of the material is changed in the unit of time. Those in which less energy is transformed proceed more slowly. The speed of the chemical change, and the quantity of energy available because of it, are closely related. Now, we are accustomed to speak of materials which, like iron and sulphur, interact rapidly and with liberation of much energy as "chemically active." Thus, **relative chemical activity** may be estimated, (1) by observing the speed of a change (see below), or, in many cases (2) by measuring the heat developed (see Thermo-chemistry, below), or (3) by ascertaining the electromotive force of the current, when the materials are arranged in the form of a battery-cell (see Chap. XXXIX).

It is evident that the chemical activity of a given substance will not be the same towards all others. Thus, iron unites much more vigorously with chlorine than with sulphur and, with identical amounts of iron, more heat is liberated in the former case than in the latter. With silver, sodium, and many other substances, iron does not unite at all. One of the tasks of the chemist is to make such comparisons as this. He calls the results the specific chemical properties of the substances in question.

The "Cause" of Chemical Activity or Affinity. — The reader will undoubtedly be inclined to inquire whether we can assign any cause for the tendency which substances have to undergo chemical change. Why do iron and sulphur unite to form ferrous sulphide, while other pairs of elements taken at random will frequently be found to have no effect upon one another under any circumstances? The answer is that we do not know. Questions like this have to go without answer in all sciences. What is the cause of gravitation? We know the facts which are associated with the word — the fact that bodies fall towards the earth, for example — but why they fall we are unable to say. So, with chemical change, we can state all the facts we know about it, but even then we cannot say *why* it takes place.

The word **cause** was employed in the heading of this section, and it will be observed that no cause was found. This is the invariable rule in physical or chemical phenomena. We know of no causes, in the sense in which the word is commonly employed.

The word cause has only one definite use in science. When we find that thorough incorporation of the three materials is needed to secure good gunpowder, we say that the intimate mixing is a cause of its being highly explosive. By this we simply mean that intimate mixture is a *necessary antecedent* of the result. A **cause is a condition or occurrence which always precedes another condition or occurrence.**

The Speed of Chemical Actions: a Means of Measuring Activity. — One means of measuring the relative chemical activities of several substances is to observe the speed with which they undergo the same chemical change. Thus we may compare the activities of the various metals by allowing them separately to interact with hydrochloric acid and collecting and measuring the hydrogen liberated per minute by each. It will be seen, even in the roughest experiment, that magnesium is thus much more active than zinc. The comparison must be made with such precautions, however, as will make it certain that the conditions under which the several metals act are all alike. Thus, in spite of the heat evolved by the action, means must be used, by suitable cooling, to keep the temperature at some fixed point during the experiment, for all actions become more rapid when the temperature rises (p. 20). Again, the pieces of the various metals must be arranged so that equal surfaces are exposed to the acid in each case. It is found that the order in which this comparison places the metals is much the same as that in which they are placed by a study of other similar actions. A single table, showing the order of activity (p. 60), suffices, therefore, for all purposes.

Thermochemistry. — Chemical changes in which heat is liberated are called **exothermal**. Those in which heat is continuously absorbed (pp. 14, 167, 113) are called **endothermal** changes. Since the activities, or affinities of two substances (say, two metals) may often be measured by observing the amounts of heat liberated when each combines with a third substance (say, oxygen), it will be instructive now to consider some of the elementary facts of thermochemistry.

The chemical interactions to be studied thermally are arranged so that they may be carried out in a small vessel which can be placed inside another containing water. The whole apparatus is called a **calorimeter** (Gk., *heat-measurer*). The heat developed raises the temperature of this water. Where gases like oxygen are concerned, a closed bulb of platinum forms the inner vessel. The quantity of heat capable of raising one gram of water one degree in temperature at 15° Centigrade is called a **calorie.** So that 250 grams of water raised 1° would represent 250 calories, and 20 grams of water raised 5° would represent 100 calories.

Thermochemical Equations. — While in physics the unit of quantity is the gram, in chemistry the unit which we select is naturally a gram-atomic weight or a gram-molecular weight of the substance. Thus, the heat of combustion of carbon means the heat produced by combining twelve grams of carbon with thirty-two grams of oxygen, and is sufficient to raise nearly 100,000 grams of water one degree. This is expressed as follows:

$$C + O_2 \rightarrow CO_2 + 96{,}820 \text{ cal.}$$

In other words, the combustion of less than half an ounce of carbon will raise over two pounds (one kilogram) of water from 0° to the boiling-point.

When the action is one which absorbs heat, this fact is indicated by the negative sign preceding the number of calories. Thus, the dissociation of 36 g. of water vapor into hydrogen and oxygen absorbs 28,800 cal. per gram of hydrogen liberated:

$$2H_2O \rightarrow 2H_2 + O_2 - 115{,}200 \text{ cal.}$$

If the action is reversible, as this one is, the heat absorbed when it proceeds in one direction is equal to that liberated when it goes in the other direction:

$$2H_2 + O_2 \rightarrow 2H_2O + 115{,}200 \text{ cal.}$$

An action which absorbs heat can take place only when heat or some other form of energy is furnished. Thus, the electrolysis of aqueous hydrochloric acid (p. 155) consumes electrical energy, which is equivalent in amount to the heat given out when hydrogen and chlorine unite to form hydrogen chloride, plus the heat liberated when the latter dissolves:

$$H_2 + Cl_2 + Aq \rightarrow 2HCl, Aq + 78{,}800 \text{ cal.}$$

Answers to Possible Questions. — It is always found that the same quantities of any given chemical substances, undergoing the same chemical change under the same conditions, produce or absorb, according as the action is exothermal or endothermal, amounts of heat which are equal.

The *rate* at which a given chemical action is allowed to take place has no influence on the total amount of heat consumed or produced. It may not at first sight appear obvious that rusting evolves heat, but a delicate thermometer will show that a heap of rusting nails is somewhat higher in temperature than surrounding bodies. Poor conductors, like oily rags and ill-dried hay, show a tendency to spontaneous combustion owing to accumulation of the slowly developing heat of oxidation (p. 37). The warmth of our own bodies is due to the same cause.

It should be noted that production or absorption of heat is not, in itself, an evidence of chemical action. Physical changes are all likewise accompanied by the same phenomena. Thus, the evaporation of water absorbs heat, and condensation of a vapor and the crystallization of a supercooled liquid liberate heat.

The **heat of solution** (*cf.* pp. 125, 145) is the heat liberated (or absorbed) on dissolving one mole of the substance in a large amount of water. A part of the water always undergoes chemical change (p. 139). The solute also frequently combines with a part of the water, or is ionized (*q.v.*), and the change in volume of the mixture (p. 138), as a physical phenomenon, would alone entail a heat-change. Hence this heat effect is partly chemical and partly physical in origin.

Exercises. — 1. Which form of energy is delivered as such, and paid for as such, in most cities?

2. How many calories are required to raise 500 g. of a substance of specific heat 0.5 from 15° to 37° (p. 174)?

3. The combustion of 1 g. of sulphur to sulphur dioxide develops 2220 calories. What is the heat of combustion of sulphur? Write the thermochemical equation.

CHAPTER XIV

CHEMICAL EQUILIBRIUM

In spite of its formidable title, this chapter will introduce nothing novel. Its purpose is to collect together and organize more definitely a number of scattered facts and ideas which have already come up in various connections. On this account, however, it will be all the more necessary for the reader to refresh his remembrance of these facts and ideas by re-reading all pages to which reference is made.

Reversible Actions. — In discussing Deacon's process (p. 156), it was stated that the action comes to rest although a large amount of *both* of the interacting substances (20 per cent at 345°) still remains available: (20 per cent) $4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2$ (80 per cent). Now the materials thus left unused are presumably no less capable of interacting than were the parts which have already reacted. The solution of this mystery lies in the fact (p. 156) that the *products themselves interact* to reproduce the initial substances (read the equation backwards). Thus two changes, one of which undoes the work of the other, are going on simultaneously. In consequence of this, neither action can reach completion. As we should expect, experiment shows that it makes no difference whether we *start* with pure chlorine and steam, or with hydrogen chloride and oxygen; the proportions of the four substances found in the tube, after it has been kept at 345° for a sufficient time, are in both cases the same. A **general statement** may be founded on facts like this, to the effect that **a chemical action must remain more or less incomplete when the reverse action also takes place under the same conditions.** Two arrows pointing in opposite directions are used in equations representing reversible changes.*

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* The reader must avoid the idea that a reversible action is one which goes to completion, and then runs back to a certain extent. This conception would be contrary to the fact, and inexplicable by the kinetic method.

The foregoing example of a reversible action, and the following examples which very closely resemble it, should now be looked up and studied attentively. The discussion in this and the following sections, for which they furnish the basis, cannot otherwise be understood: (1) the interaction of chlorine and water (p. 161), which was fully discussed at the time; (2) the behavior of phosphorus pentachloride vapor (p. 117); (3) the behavior of water vapor (p. 93), of phosphorus vapor (p. 117), of sulphur vapor (p. 117), and of iodine vapor (p. 117).

When the action is one which is reversible, but, under the circumstances being discussed, proceeds farther towards completion in one direction than in the other, the arrow will be modified to indicate this fact:

$$\mathrm{Cl_2 + H_2O \rightleftarrows HCl + HClO}\ \text{(p. 161)}.$$

When this relative completeness is due to precipitation or volatilization, the fact may be indicated by vertical arrows:

$$\mathrm{NaCl + H_2SO_4 \rightleftarrows NaHSO_4 + HCl}\uparrow\ \text{(p. 141)}.$$
$$\mathrm{NaCl}\downarrow \mathrm{{}+ H_2SO_4 \rightleftarrows NaHSO_4 + HCl}\ \text{(p. 143)}.$$

Actions Which Proceed to Completion. — All chemical actions do not belong to the reversible, incomplete class. Many proceed uninterruptedly to exhaustion of one, or all, of the ingredients. For example, equivalent amounts of magnesium and oxygen combine completely, $\mathrm{2Mg + O_2 \rightarrow 2MgO}$. Here, however, the product is not decomposed even at the white heat produced by the vigor of the union. Indeed, magnesium oxide cannot be decomposed, and the action reversed, at any temperature we can command. The other **complete actions,** like the decomposition of potassium chlorate (p. 27), **are so because they are** likewise **irreversible.**

Explanation in Terms of Molecules. — Restating these facts in terms of the molecules will enable us to reason more clearly about this variety of chemical change. Suppose we start with the materials represented on *one side* only of such an equation, say the hydrogen chloride and oxygen in that on p. 177. The molecules of these materials will encounter one another frequently in the course of their movements. In a certain proportion of these collisions the chemical change will take place. In the earliest stages there will be few of the new kind of molecules (say, of chlorine and steam), but, as the action goes on, these will increase in number. There will be two consequences of this. In the first place the parent materials (in this case, hydrogen chloride and oxygen) will diminish in amount, the collisions between their molecules will become fewer, and the speed of the forward action will therefore become less and less. In the second place the increase in the number of molecules of the products will result in more frequent collisions between them, in more frequent occurrence of the chemical change which they can undergo, and thus in an increase in the speed of the reverse action. The forward action begins at its maximum and decreases in speed progressively; the reverse action begins at zero and increases in speed. Finally the two speeds *must become equal*, and at that point perceptible change in the condition of the whole must cease (*cf.* pp. 88–89).

The most immediate inference from this mode of viewing the matter is, that the apparent halt in the progress of the action does not indicate any cessation of either chemical change. Both changes must go on, in consequence of the continued encounters of the proper molecules. But since the two changes proceed with *equal speeds* they produce no alteration in the mass as a whole. In fact, the final state is one of equilibrium, and not of rest, one of balanced activity and not of repose. Hence, chemical changes which are reversible lead to that condition of seemingly suspended action which we speak of as **chemical equilibrium.**

Chemical Equilibrium and its Characteristics. — The detailed discussion of the relations of liquid and vapor (pp. 78, 87–90), and of saturated solution and undissolved solid (pp. 127, 130–133), has already familiarized us with the term equilibrium and its significance. We can, in fact, apply to the discussion of any kind of reversible phenomena, the sets of ideas in regard to exchanges of molecules there elaborated.

In particular, the reader will note that the **three characteristics of a state of equilibrium,** developed and illustrated in the case of the physical equilibrium between a liquid and its vapor (p. 89), apply also to a typical case of chemical equilibrium, such as that in Deacon's process now before us. Thus:

1. There are **the two opposing tendencies, which ultimately balance one another.** Here they are the tendency of the steam and chlorine to produce hydrogen chloride and oxygen, and the tendency of the hydrogen chloride and oxygen to reproduce steam and chlorine by this interaction. In other words, they are the **apparent activity** of the hydrogen chloride and oxygen interaction, and the **apparent activity** * of the steam and chlorine reaction.

2. **At equilibrium the two opposing tendencies or activities are still in full operation,** although their effects then neutralize one another.

3 (and this is the chief mark of chemical, as it is of physical equilibrium). The system is in a sensitive state, so that **a change in the conditions** (temperature and pressure or concentration), even if slight, **produces a corresponding change in the state of the system, and does this by favoring or disfavoring one of the two opposing tendencies or apparent activities.** Such a change is called **a displacement of the equilibrium,** for the system settles down in a new state of equilibrium with new proportions of the two sets of substances, corresponding to the changed conditions. Thus, in the present instance, a change from 345°, where there is 80 per cent of the material in the form of steam and chlorine, to 384° results in the diminution of this proportion to 75 per cent. The equilibrium is affected by changes in concentration also, as we shall presently see (pp. 181, 186).

Now, the foregoing facts show that the key to understanding chemical activities, their magnitudes, their changes, and especially their practical results, *must lie in knowing how changes in the conditions affect them.* Hence, to the chemist, familiarity with the influence of conditions on chemical phenomena must be of the greatest practical importance. We therefore address ourselves to the discussion of this subject.

The "conditions" to be considered are familiar, — temperature, and concentration or, in the case of a gas, partial pressure. The "activity" of an action is accurately measured by the speed with which the action proceeds. Thus, if the foregoing section be re-examined, it will be seen that we spoke throughout of the *speed*, rather than of the tendency or activity.

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* We use the term "apparent activity" for the activity as we see it. In the same action it varies with the conditions. The **intrinsic activity** or **affinity,** on the other hand, is the absolute activity of the action *irrespective of conditions.* Its value can be determined only by eliminating the effect of conditions, a matter which is too abstract for consideration here. The apparent activity is the practical thing which we observe.

Finally, temperature and other conditions influence also the activities in, and therefore the speeds of, those actions which proceed to completion, and are not reversible. Hence, unless our statements are expressly restricted to reversible actions and to states of equilibrium, they apply to all chemical changes.

The Influence of Concentration. — In the first place, let us assume that the temperature is constant, and let us confine our attention for the present to the influence of concentration upon a chemical reaction. We have seen (p. 178) that the speed of a chemical change is determined by the frequency with which the molecules of the interacting substances encounter one another. The frequency of the encounters amongst a given set of molecules, resulting in a definite chemical change, will in turn evidently depend entirely upon the degree to which the molecules are concentrated in each other's neighborhood. Larger amounts of one of the materials, for example, will not result in more rapid chemical action, if the larger amount of material is also scattered through a larger space. Chemical changes, therefore, are not accelerated by increasing the mere quantity of any ingredient, but only by increasing the **concentration of its molecules.** Thus, a large amount of hydrochloric acid with a piece of zinc will generate hydrogen no faster than a smaller amount. But substitution of more concentrated acid will instantly increase the speed of the action. In the second case, the number of molecules of the acid reaching the zinc per second is greater, and this action, being non-reversible, proceeds more rapidly to complete consumption of the zinc. So also, iron burns faster in oxygen (100 per cent) than in air (20 per cent oxygen).

With a reversible action the effect on the speed is the same, excepting that the continued activity of the reverse action prevents the direct one from reaching completion.

Thus, if, in the action of hydrogen chloride upon oxygen, we introduce *into the same space* an extra amount of *oxygen*, this facilitates the formation of steam and chlorine by increasing the possibilities of encounter between molecules of hydrogen chloride and oxygen. At the same time it does not affect (*cf.* p. 72) the number of encounters in a given time of steam and chlorine molecules with one another which result in the reverse transformation. The proportion of chlorine (and steam) formed, therefore, from a given amount of hydrogen chloride will be greater, although the total possible (by complete consumption of the materials) has not been altered, since the quantity of one ingredient only has been increased. The introduction of an excess of hydrogen chloride would have had precisely the same effect.

An Experimental Illustration. — A reaction in which the effects of different concentrations were carefully studied by Gladstone (1855) affords a good illustration. If ferric chloride and ammonium thiocyanate are mixed in aqueous solution, a liquid containing the soluble, *blood-red* ferric thiocyanate is produced. The compound radicals are (NH_4) and (CNS), and the action is a simple double decomposition:

$$FeCl_3 + 3\,NH_4CNS \rightleftarrows Fe(CNS)_3 + 3\,NH_4Cl.$$

The action is a reversible one, and the mixture is homogeneous, *i.e.*, there is no precipitation. Now, if the two just-named salts are mixed in very dilute solution in the proportions required by the equation, say by adding 20 c.c. of a decinormal solution (p. 124) of each salt to several liters of water, a pale-reddish solution is obtained. When this is divided into four parts, and one is kept for reference, the addition of a little of a concentrated solution of ferric chloride to one jar, and of ammonium thiocyanate to another, will be found to deepen the color by producing more of the ferric thiocyanate. On the other hand, mixing a few drops of concentrated ammonium chloride solution with the fourth portion will be found to remove the color almost entirely, on account of its influence in accelerating the backward change.

The Law of Molecular Concentration. — The general principle discussed and illustrated in this section may be called **the law of molecular concentration,** and may be stated as follows: **In every chemical change the apparent activity, and therefore the speed of the action, is proportional to the molecular concentration of each interacting substance.** This holds whether the action is reversible or not.

We shall next give a more precise, semi-mathematical formulation of this law, as this formulation will be of use later,* and then proceed to illustrate the application of the law, by showing how it explains large classes of actions of which we have already encountered many examples.

Formulation of the Law of Molecular Concentration.— The mathematical formulation of the law describing the influence of the concentration of the molecules of each participating substance upon the speed of the action is extremely simple. When the actual concentrations of the molecules are specified (in moles, pp. 102, 125, per liter), and the speed is suitably expressed (in moles transformed per minute or per hour), we find that the speed is proportional to the concentration of each molecule appearing in the molecular equation for the action. Thus in the interaction of hydrochloric and hypochlorous acids (the reverse of the action of chlorine on water, pp. 161, 178), if [HCl] and [HClO] represent the concentrations of the molecules HCl and HClO, and k is a constant, and S is the speed, then

$$[\mathrm{HCl}] \times [\mathrm{HClO}] \times k = S.$$

Again, for the dissociation of phosphorus pentachloride vapor into phosphorus trichloride and chlorine (p. 117): $PCl_5 \rightarrow PCl_3 + Cl_2$, if $[PCl_5]$ represents the concentration of the PCl_5 molecules, k_1 is a constant, and S_1 is the speed of decomposition:

$$[\mathrm{PCl_5}] \times k_1 = S_1.$$

Similarly, for the reverse action: $PCl_3 + Cl_2 \rightarrow PCl_5$, if $[PCl_3]$ and $[Cl_2]$ stand for the molecular concentrations of these substances:

$$[\mathrm{PCl_3}] \times [\mathrm{Cl_2}] \times k_2 = S_2.$$

The constant has a different value in each separate action. It includes the value of the intrinsic affinity or activity of the substances, and the catalytic effect (p. 29), if any, of the materials present.

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* This formulation of the law is not required, or referred to in the sections which follow. The section and the following one may therefore be omitted for the present and be taken up in connection with Chaps. XX and XXXV.

Formulation of the Condition for Chemical Equilibrium. — The foregoing plan may be used further to formulate **the condition for chemical equilibrium.** As we have seen (p. 179), a characteristic of a system in chemical equilibrium is that the speeds of the forward and reverse actions have become equal. If, then, $[PCl_5]_{eqm.}$, $[PCl_3]_{eqm.}$, and $[Cl_2]_{eqm.}$ now represent the molecular concentrations when the system has reached *equilibrium*, then, since the speeds are equal:

$$[PCl_3]_{eqm.} \times [Cl_2]_{eqm.} \times k_2 = [PCl_5]_{eqm.} \times k_1,$$

$$\frac{[PCl_3]_{eqm.} \times [Cl_2]_{eqm.}}{[PCl_5]_{eqm.}} = \frac{k_1}{k_2} = \text{constant}.$$

In words, this means that if we change the amount of the pentachloride placed in the vessel, or if we use amounts of chlorine and trichloride which are not equivalent, the numerical value at equilibrium of each concentration ($[PCl_3]$ etc.) will, of course, be different, but the product of the concentrations of trichloride and chlorine, divided by the concentration of the pentachloride, will always give the same numerical value for the constant at the same temperature. This numerical value is called the **equilibrium constant.**

Applications: The Forward Action. Homogeneous and Inhomogeneous Systems. — While there are all degrees of speed in chemical actions, yet in practice we quickly distinguish two different classes. There is a class of actions of which most examples are almost instantaneously accomplished, and a class in which, frequently, the operation takes minutes or even hours. The classes overlap, but, in a general way, the following distinction may be made.

To the former, speedy class belong the explosion of hydrogen and oxygen or other gaseous mixtures, and the interactions when solutions are mixed, as in precipitations. In view of the foregoing explanations, we perceive that the **rapid accomplishment of** such **actions is due,** not so much to any especially great intrinsic affinity, as **to the homogeneous state of mixture of the interacting materials.** This, of course, is a purely physical, and not a chemical motive for speedy interaction. In intimate mixtures, every molecule has an equal opportunity freely to encounter every other molecule and there is therefore no mechanical impediment to the operation of the affinities of the substances. Hence the apparent activity is great.

To the second class, comprising the slower actions, belong cases like the interaction of a piece of zinc with hydrochloric acid, or of manganese dioxide (p. 158) with the same acid, whereby hydrogen and chlorine, respectively, are slowly evolved, and the solid is gradually consumed. Here the hindrance is evidently the fact that the interacting substances are not intimately mixed. **In the slow actions, the system is inhomogeneous.** Pulverizing the solid before use will increase the speed, indeed, by providing more surface and better mutual contact, but will not transfer the action to the rapid class. It is chiefly the *dissolved* part of the substance which interacts, for chemical action takes place between molecules, and only the dissolved part is disintegrated in such a way that the molecules are readily accessible. Thus, the action is held back by continual waiting for the slow replenishment, from the "insoluble" solid, of the supply of dissolved molecules. In the cases cited, the restraining influence of the dissolving process, which is part of the whole phenomenon, may be formulated thus:

$$\mathrm{Zn(solid)} \leftrightarrows \mathrm{Zn(dslvd)} + 2\mathrm{HCl} \rightarrow \mathrm{ZnCl_2} + \mathrm{H_2}.$$
$$\mathrm{MnO_2(solid)} \leftrightarrows \mathrm{MnO_2(dslvd)} + 4\mathrm{HCl} \rightarrow \mathrm{MnCl_2} + 2\mathrm{H_2O} + \mathrm{Cl_2}.$$

Here, again, the mechanical details, depending on physical properties, have more to do with the progress of the action than has the chemical affinity. In terms of the law of concentration, the action is slow, and the apparent activity small, because the concentration of the acting molecules of one of the substances is very small, and cannot be increased because of low solubility.

Applications: The Reverse Action. Displacement of Equilibria. — We have seen (p. 182) that one way in which a reversible action may be forced nearer to completion, in one direction or the other, is the introduction of an excess of one of the ingredients contributing to the forward action. This method of displacing the equilibrium point, however, cannot be very effective, unless it is possible to introduce an exceedingly large excess of the selected ingredient in a high degree of molecular concentration, since this operation *does not in any way affect or, in particular,* *restrain the reverse action* which is continually undoing the work of the forward one. A much more effective **means of furthering the desired direction of such actions is found,** therefore, **in the restraint or practical annulment of the reverse action.** A good way of accomplishing this is to **allow the products of the direct action to separate into an inhomogeneous mixture.** Any agency which could remove the water vapor as fast as it was formed by the interaction of hydrogen chloride and oxygen, for example, would entirely stop the reproduction of these substances, and so would enable the forward action ($4HCl + O_2 \rightarrow 2H_2O + Cl_2$) to run to *completion.*

This might be realized by causing one end of a sealed tube charged with the substances, after the contents had settled down to a condition of equilibrium, to project from the bath in which the whole had been kept at 345° (Fig. 74, which is simply diagrammatic). By cooling this end, a large part of the steam would quickly be condensed in it to the liquid form, while the other substances would remain gaseous. In other words, the concentration of the water vapor would be greatly reduced. In fact, only the trace of vapor which cold water gives would then be available to interact with the chlorine, and reproduce hydrogen chloride. Meanwhile the decomposition of the latter would go on, and thus, eventually, almost all the water would be found in one end of the tube, and the chlorine, all free, would occupy the rest. By this purely mechanical adjustment the chemical change would therefore be carried from 80 per cent completion to almost absolute completion:

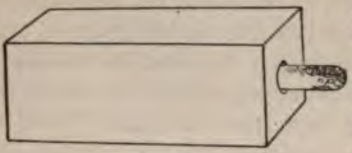
FIG. 74.

$$4HCl + O_2 \rightleftarrows 2Cl_2 + 2H_2O \text{ (vapor)} \rightleftarrows 2H_2O \text{ (liq.)}$$

If, on the other hand, arrangements were made to have powdered marble, in a sealed bulb of thin glass, enclosed in the tube, we might imagine the very opposite of the above effect to be produced. The breaking of the bulb of marble, when equilibrium had been reached, would provide means for the removal of all the hydrogen chloride,* while the other three substances would still be

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* The hydrogen chloride would be destroyed by interaction with the marble:

$$2HCl + CaCO_3 \rightarrow CaCl_2 + CO_2 + H_2O.$$

The calcium chloride is a solid. The gas, carbon dioxide, does not interact with the other substances, and would not, therefore, interfere with the formation of fresh hydrogen chloride.

gaseous. Thus, the compound (HCl) having been reduced in concentration to the point of being removed entirely, there would be no direct action to undo the work of the reverse action. The whole chlorine would, therefore, soon have passed through the form HCl. Hence, by another mechanical arrangement, an action which ordinarily could progress to only 20 per cent would be turned into a complete one:

$$2Cl_2 + 2H_2O \rightleftarrows 2H_2O + 4HCl\ (+CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2).$$

Reversibility Usually Avoided. — In every-day chemical work, since our object is usually to prepare some one substance, chemists either avoid chemical changes which are notably reversible, or adjust the conditions, as is done in the foregoing illustrations, so that the reverse of the action which they desire is prevented. In consequence of this, when carrying out the directions for making familiar preparations, the fact that such actions are reversible at all very readily escapes our notice. Arranging the conditions so that the separation of a solid body by precipitation, or the liberation of a gas, takes place, are the two commonest ways of rendering a reversible action complete. Excellent examples of both of these are furnished by the chemical change used in producing hydrogen chloride by the interaction of salt and sulphuric acid, the full discussion of which (p. 142) should now be studied attentively in the light of these explanations.

History. — The conceptions discussed in this chapter are not new, although they have come into general use rather recently. The law of reaction speed, and the influence of the concentrations of the reacting substance thereon (p. 183), was set forth and formulated by Wilhelmy as early as 1850. Gladstone (1855) studied quantitatively the influence of concentration in cases of chemical equilibrium (p. 182). The kinetic explanation (p. 178) was developed by Williamson (1851). Finally, the laws of chemical equilibrium were formulated more explicitly and applied more thoroughly by two Swedish chemists, Guldberg and Waage (1864–9).

The Influence of Temperature on the Speed of any Reaction. — The activity of chemical change, and therefore the

speed of all chemical changes, is increased by raising the temperature and diminished by lowering it (*cf.* p. 59). Thus, zinc displaces hydrogen more rapidly from hot than from cold hydrochloric acid. Different actions are affected in different degrees, and no simple rule accurately defining the effect can be given. Roughly speaking, however, a rise of 10° doubles the speed of every action. A rise of 100° will therefore make the speed roughly 1024 times greater. Hence, when the chemist finds that two substances show no evidence of interaction, he infers that there must be either slow action or none, and he seeks to settle the question quickly by heating the mixture.

The Influence of Temperature on a System in Equilibrium. — In a reversible change the two opposing reactions *are different actions* and their speeds are therefore affected *in different degrees* by the *same* alteration in temperature. Hence, when the temperature is changed, the relative amount of the two sets of materials present is altered and the equilibrium is displaced. Thus, in Deacon's process, a rise of 40° in the temperature displaces the equilibrium backwards (p. 180), and diminishes the yield of chlorine by 5 per cent. In the vapor of phosphorus pentachloride (p. 117), the displacement is in the opposite direction. The vapor is a mixture of the pentachloride with the trichloride and free chlorine: $PCl_5 \rightleftarrows PCl_3 + Cl_2$. At 200°, 51.5 per cent of the material is present as pentachloride and 48.5 per cent as trichloride and chlorine. Raising the temperature to 250° changes the proportions to 20 per cent and 80 per cent, respectively. At 300° only 3 per cent of the pentachloride remains. Evidently, here, raising the temperature favors the decomposition of the pentachloride, and therefore increases the speed of its dissociation more than it does the speed of the reunion of the trichloride and chlorine.

Van't Hoff's Law. — One use of a law is to enable us to answer a question, when we have not in memory the fact constituting the answer, and even when we have never read or heard the fact. The law or rule enables a little reasoning to take the place of a vast amount of memorizing. Thus, to answer the question: Does sodium chloride always have the same composition, it is not necessary to have read and to remember all, or any of the numerous investigations of this substance that have been made. We simply refer the question, mentally, to the law of definite proportions, and say "yes." Now the facts mentioned above are connected by a law which will answer many practical questions in chemistry.

When phosphorus trichloride and chlorine combine (to form PCl_5), *heat is given out.* Conversely, when phosphorus pentachloride dissociates, *heat is absorbed:*

$$PCl_5 + 30{,}000 \text{ cal.} \rightleftarrows PCl_3 + Cl_2.$$

Now, when the temperature is *raised,* the action proceeds in the direction of decomposing more of the pentachloride. That is, the equilibrium is displaced in the direction which *absorbs heat.*

In Deacon's process, we find that the interaction of hydrogen chloride and oxygen *liberates heat,*

$$4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2 + 28{,}000 \text{ cal.},$$

and in this action *raising* the temperature drives the equilibrium backwards, and a *lowering* in the temperature is required to increase the yield of chlorine.

The rule is obvious, and applies to all reversible reactions: **When the temperature of a system in equilibrium is raised, the equilibrium point is displaced in the direction which absorbs heat.** In other words, a rise in temperature favors the interaction of that one of the two sets of materials to which the heat is *added* (+ sign) in the equation. If the equation happens to be written with a negative heat of reaction (*e.g.*, p. 175), the heat can, of course, be transferred to the other side with its sign changed. This law is known as **Van't Hoff's law of mobile equilibrium.**

This law is of practical value. More than once, in chemical factories, much time and money have been spent on trying to arrange machinery to give a better yield of some substance at a high temperature, when a reference to this law would have shown that the chief change necessary was to use a lower temperature. We shall frequently have occasion to refer to this law.

Application to Physical Equilibria. — Van't Hoff's law applies also to physical processes. Thus, as the temperature rises, a substance which absorbs heat in dissolving will become more soluble. This is the commoner case, as is shown by the way in which most solubility curves (Fig. 58, p. 131) ascend with rising temperature. Conversely, a substance which gives out heat in dissolving is *less* soluble with rising temperature in a solution already almost saturated with the compound. For example, anhydrous sodium sulphate gives out heat in dissolving, and so its solubility diminishes (Fig. 59, p. 132), with rising temperature.

Again, the vaporization of a liquid absorbs heat, and so an increase in temperature will increase the pressure, and therefore the concentration of its vapor (p. 87).

Le Chatelier's Law. — The above mentioned law is really a particular case of a more general one. **If some stress** (*e.g.*, by change of temperature, pressure, or concentration) **is brought to bear on a system in equilibrium, the equilibrium is displaced in the direction which tends to undo the effect of the stress.** Thus, raising the temperature furthers the change which absorbs heat — and therefore would tend to lower the temperature. Increasing the concentration of the molecules pushes the action in the direction which uses up these very molecules (p. 181). Again pressure causes ice to melt, because the water which is formed occupies a smaller volume, and this change tends to relieve the pressure. But pressure will not cause most substances to melt, because usually the liquid form occupies a greater volume and its production would tend to increase pressure.

Summary. — In this chapter we have answered three questions:

1. Why do some chemical actions cease, while still incomplete? Answer: They are reversible.
2. What explains the position of the equilibrium point? Answers: (*a*) Equal effects of opposed molecular actions; (*b*) Equality in speed of opposed reactions.
3. What will displace the equilibrium point? Answer: (*a*) Change in concentration of one (or more) of the substances; (*b*) Change in the temperature.

Exercises. — 1. Explain the completeness of the action by which hydrogen chloride and water, respectively, are formed by direct union of the elements.

2. Explain the completeness of the action by which silver chloride (p. 148) is formed.

3. Explain why the decomposition of potassium chlorate is complete.

4. In view of the statement on p. 14, explain why mercuric oxide is completely decomposed by heating. Point out the resemblance between this experiment and the imaginary one illustrated in Fig. 74 (p. 186).

5. Why can magnetic oxide of iron be reduced completely by a stream of hydrogen (p. 59), and iron oxidized completely by a current of steam (p. 51)?

6. With the phosphorus pentachloride system, say at 250°, what effect would suddenly enlarging the space containing a given amount of the vapor produce? What would be the effect of diminishing the space? What would be the effect of introducing additional chlorine into the same space (p. 181)?

7. By what practical means could the degree of dissociation of sulphur vapor (S_8) be reduced, without changing the temperature (p. 117)?

8. What inference should you draw from the fact that: (*a*) the solubilities of potassium nitrate and of Glauber's salt (p. 132) increase with rise in temperature; (*b*) that those of calcium hydroxide (p. 130) and triethylamine decrease with rise in temperature?

CHAPTER XV

THE HALOGEN FAMILY

THE elements to which we have so far devoted most attention have been oxygen, hydrogen, and chlorine. If we recall the chemical properties and relations of these elements we shall recognize the fact that they all possess very distinct individualities.

The Chemical Relations of Elements. — Hydrogen is a substance (p. 58) which unites readily with oxygen and chlorine, less readily with other non-metals, and scarcely at all with metals. Oxygen and chlorine resemble each other somewhat in the greatness of their chemical activity and the variety of free elements with which they are capable of uniting, but differ markedly in what we have called their chemical relations (p. 163). The resulting compounds belong, in fact, to quite different classes — oxygen forms oxides, chlorine forms chlorides — **and elements are considered similar only when they resemble each other in chemical relations, and produce, by combination with the same element, compounds having similar chemical properties.** Thus, the common oxide of hydrogen, water, is a neutral substance, and is chemically rather indifferent. The chloride of hydrogen in aqueous solution is a strong acid and is chemically very active.* If all the other chemical elements differed from one another as much as do these three, they would be incapable of classification. In reality, however, we find that the elements can be grouped together in sets. They are classified according to the kind of substances with which they combine and the chemical nature of the products. In some families the resemblance is close, in others less close. The present group is of the former class, and will serve, therefore, as a convenient beginning in the work of tracing relations between the elements and in classifying the facts of descriptive chemistry.

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* The difference between oxides and chlorides is seen in their behavior. Thus, oxides often unite with water to form acids or bases (p. 94). Chlorides do not unite with water to form new substances with marked characteristics (*cf.* p. 96).

The Chemical Relations of the Halogens. — The bromide ($NaBr$), iodide (NaI), and, to a less extent, the fluoride (NaF) of sodium, resemble sodium chloride ($NaCl$) in appearance and behavior. From this fact, chlorine, bromine, iodine, and fluorine are known as the **halogens** (Gk., *salt producers*), and their compounds are named the **halides**. The halogens, as the above formulæ show, are univalent. They all form compounds with hydrogen, and these compounds closely resemble hydrogen chloride. For example, they are colorless, they are gases (except hydrogen fluoride, a very volatile liquid), they are very soluble in water, and their solutions are acids. Other relations will be given in a summary at the end of the chapter.

BROMINE Br_2

Occurrence. — The compounds of chlorine, bromine, and iodine usually occur together in nature, while the compounds of fluorine are not found in the same sources. Bromine occurs chiefly in the form of the bromides of sodium and magnesium, in the upper layers of the natural beds of rock salt. Liebig made it from this source and a little later Ballard (1826) made it also and recognized it as a new element.

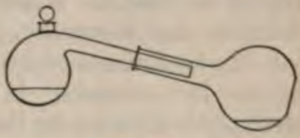


FIG. 75.

Preparation. — In the chemical point of view there are three distinct ways in which bromine is made. 1. The first of these is closely related to the common method of preparing chlorine (p. 158). As hydrobromic acid, unlike hydrochloric acid, is not formed extensively in connection with any chemical industry, potassium bromide is treated in a retort (Fig. 75) with concentrated sulphuric acid, and the product is oxidized with powdered manganese dioxide in one operation. (For equation see next section.) Bromine being a volatile liquid, while the sulphates of potassium and manganese are involatile, its vapor passes off when the above mixture is heated. It is condensed in a flask surrounded by cold water.

2. The second method of preparing bromine depends on the fact that chlorine is a more active element and *displaces* bromine from combination. When, therefore, chlorine is passed into a solution of potassium or sodium bromide, potassium or sodium chloride is formed and the bromine liberated:

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2.$$

When the liquid is warmed, the bromine passes off along with a part of the water, and may be condensed as before.

3. Aqueous solutions of soluble bromides may be decomposed by means of a current of electricity. The bromine is set free at the positive electrode.

Commercial Extraction. — Two-thirds of the world's supply is obtained from Stassfurt, where, after the extraction of the potassium chloride from the impure **carnallite** ($KCl,MgCl_2,6H_2O$), the mother-liquor is found to contain the more soluble sodium and magnesium bromides in considerable quantities. The warm mother-liquor trickles down over round stones in a tower. The chlorine is introduced from below and dissolves in the liquid. The bromine is thus liberated and passes off as vapor. A part of our supply of bromine is obtained from the brines of Ohio, West Virginia, and Kentucky, from which, after most of the common salt has been removed by crystallization, the bromine is obtained by the first method. In Michigan the brines are treated with electrolytic chlorine by the second method.

Partial Equations, a Plan for Making Complex Equations. — When an equation involves *more than two* initial substances or products, as does the one for the first method of preparing bromine, it cannot readily be worked out by the method formerly recommended (p. 51). After the formulæ of all the substances, on both sides, have been set down, it is difficult to hit upon the proper coefficients required to balance the equation. In such cases, a good plan is to select *two* of the initial substances, and make a **partial equation** showing part of the action and including at least one actual product. Any unused units (not constituting a product) are then set down also and treated as a balance. Thus the first two of the substances named will furnish potassium-hydrogen sulphate:

Partial, 1: $KBr + H_2SO_4 \rightarrow KHSO_4\ (+ HBr).$ (1)

Similarly, the manganese dioxide and sulphuric acid will give manganous sulphate:

Partial, 2: $MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O\ (+ O).$ (2)

We then perceive that the bromine must come from the oxidation of the first balance (HBr) by the second (O):

Partial, 3: $(2HBr) + (O) \rightarrow H_2O + Br_2.$ (3)

The third partial equation shows that 2HBr will be needed for the amount of O obtainable from MnO_2, so we go back to (1) and multiply it by two throughout:

$$\begin{array}{rr}
2KBr + 2H_2SO_4 \rightarrow 2KHSO_4\ (+ 2HBr). & (1) \\
MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O\ (+ O). & (2) \\
(2HBr) + (O) \rightarrow H_2O + Br_2. & (3) \\
\hline
\multicolumn{2}{r}{2KBr + 3H_2SO_4 + MnO_2 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + Br_2.}
\end{array}$$

When we now add the real substances used and produced, as they occur in these partial equations, and leave out the balances, which have been adjusted so as to cancel one another, we obtain the final equation for the action. It must be observed that this subdivision of the action into parts is a purely arithmetical device. It is still true, however, that we are aided in the selection of partial actions at each step by following some plausible theory as to stages for the action which would be chemically conceivable.

Physical Properties. — Bromine is a dark-red liquid (sp. gr. 3.18). It boils at 59°, forming a deep-red vapor, and even at ordinary temperatures gives a high vapor pressure (150 mm. at 18°) and evaporates quickly. When cooled it forms red, needle-shaped crystals (m.-p. − 7.3°). A saturated aqueous solution (**bromine-water**) contains 3 parts of bromine in 100 parts of water. The element is much more soluble in carbon disulphide, alcohol, and other organic solvents. Up to 750°, the G.M.V. weighs 160 g. (corresponding to Br_2), against 28.955 g. for air.

Bromine (Gk., *a stench*) has a most pungent odor. It has a very irritating effect on the mucous membrane of the nostrils and throat. If spilled upon the hands it destroys the tissues and leaves sores which are liable to infection.

Free bromine has no effect upon starch emulsion (see Iodine).

Chemical Properties. — A jet of hydrogen gas burns in bromine vapor. The union is much slower than in the case of chlorine (Heat of formation, + 12,300 cal.).

Bromine forms compounds directly, both with non-metals, like phosphorus and arsenic, and with most of the metals, which catch fire when thrown into the vapor. In all cases the interaction is less violent than when chlorine is used, and bromine is displaced from combination with hydrogen and with the metals by free chlorine.

Silver bromide is the sensitive material in photographic plates, and potassium and sodium bromides are **used** as sedatives in medicine. Bromine is employed in the preparation of organic dyes.

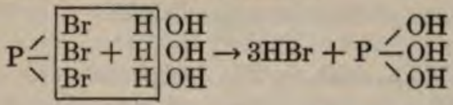
HYDROGEN BROMIDE HBr

Preparation. — It might be expected that the most convenient way of producing this compound would be similar to that used in preparing hydrogen chloride, namely, by the action of concentrated sulphuric acid upon some common bromide, such as potassium bromide ($KBr + H_2SO_4 \rightleftarrows HBr + KHSO_4$). Hydrogen bromide being less stable, however, a large part of it is oxidized by the sulphuric acid and the product is mixed with sulphur dioxide and free bromine.

$$H_2SO_4 + 2HBr \rightarrow 2H_2O + SO_2\uparrow + Br_2\uparrow .$$

Since all acids decompose all salts more or less, use of an acid which does not give up its oxygen so readily, such as phosphoric acid, will yield pure hydrogen bromide ($KBr + H_3PO_4 \rightarrow HBr\uparrow + KH_2PO_4$). The small solubility of the salt in concentrated phosphoric acid retards the interaction and makes the evolution of the gas very slow, however.

Pure hydrogen bromide is best prepared by the action of water upon phosphorus tribromide (see Hydrolysis, below). When bromine and phosphorus are mixed, a violent union of the two elements takes place, producing phosphorus tribromide PBr_3. This substance, which is a colorless liquid, is in turn broken up with great ease by water, producing phosphorous acid, which is not volatile, and gaseous hydrogen bromide:



$$\mathrm{P}\begin{array}{l}\diagup\\ -\\ \diagdown\end{array}\boxed{\begin{array}{lcr}\mathrm{Br} & & \mathrm{H}\\ \mathrm{Br} & + & \mathrm{H}\\ \mathrm{Br} & & \mathrm{H}\end{array}}\begin{array}{l}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{array} \rightarrow 3\mathrm{HBr} + \mathrm{P}\begin{array}{l}\diagup \mathrm{OH}\\ - \mathrm{OH}\\ \diagdown \mathrm{OH}\end{array}$$

In practice, these two actions are carried on simultaneously. To diminish the vigor of the interaction, red phosphorus is taken instead of yellow, and is mixed with two or three times its weight of sand in a flask (Fig. 76). A small quantity of water is added. Excess of water must be avoided, as the hydrogen bromide produced is extremely soluble, and would therefore be retained in the flask instead of being disengaged as gas. The bromine is placed in the dropping funnel, and admitted, a little at a time, to the mixture. The gas produced is passed through a U-tube containing red phosphorus mixed with glass beads. The phosphorus combines with any free bromine carried along with the gas. The second U-tube, containing water, may be attached when a solution of the gas is required. The gas may be collected in a jar by upward displacement of air.

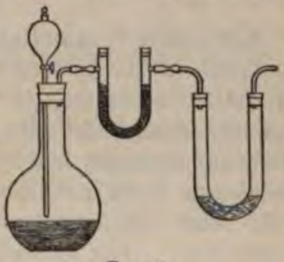


FIG. 76.

Hydrolysis. — The interaction of water with phosphorus tribromide (foregoing section) illustrates an important property of water (p. 92). The action is **a double decomposition in which water is one of the interacting substances** and is called **an hydrolysis** (Gk., *loosening by water*). The water divides into the radicals H and OH, and the former unites with the more active non-metal in the substance (the bromine, in PBr_3) and the hydroxyl with the other element. For example, $PCl_3 + 3HOH \rightarrow P(OH)_3 + 3HCl$. All the halides of the non-metals are thus hydrolyzed, as are also some other classes of compounds.

Physical Properties. — Hydrogen bromide is a colorless gas with a sharp odor. It is two and a half times as heavy as air. It is easily reduced to the liquid condition (b.-p. – 69°). It is exceedingly soluble in water, and in contact with moist air condenses the water vapor to clouds of liquid particles. Pure hydrogen bromide, whether in the gaseous condition or in the liquefied form, is a nonconductor of electricity (see below).

Chemical Properties. — The properties are like those of hydrogen chloride (p. 145). It is somewhat less stable, and dissociation begins to be noticeable at 800°. When free from water, it is not an acid (see below). The gas interacts vigorously with chlorine, hydrogen chloride and free bromine being produced, $2HBr + Cl_2 \rightarrow 2HCl + Br_2$. What are the relative volumes (p. 150)?

Chemical Properties of Hydrobromic Acid HBr, Aq. — The solution of the hydrogen bromide in water is an active acid (*cf.* p. 52). It conducts electricity extremely well. In contact with certain metals, and with oxides of metals and hydroxides of metals, it behaves exactly like hydrochloric acid (p. 146). In the first case, hydrogen is set free and the bromide of the metal produced. In the other two cases, water and the bromides of the metals are produced. For example: $Zn(OH)_2 + 2HBr \rightarrow ZnBr_2 + 2H_2O$. Oxidizing agents set bromine free from hydrobromic acid, even sulphuric acid, which does not act upon hydrochloric acid, being able to do this (p. 196). Chlorine dissolved in water displaces bromine from hydrobromic acid and from soluble bromides with ease (*test* for bromides).

IODINE I_2

Occurrence. — Iodine occurs in sea-water, about one-fifth of it in algæ and four-fifths in organic compounds. Certain species of sea-weed, known in Scotland as kelp and in Normandy as *varec,* remove it from the water. The ash of the sea-weed sometimes contains as much as two per cent, or even more. The other chief source of iodine is in Chile saltpeter (mainly $NaNO_3$), in which it is present in the form of about 0.2 per cent of sodium iodate $NaIO_3$ and sodium iodide. Most of the iodine of commerce is obtained from this source and only a little from sea-weed. The largest proportion of iodine in the human body is in the thyroid gland. In diseases like goitre and cretinism, where the thyroid is ill-developed, injection of a substance called **iodothyrine**, extracted from sheep's thyroids, produces marked improvement.

Preparation. — 1. In factories where the iodine is extracted from sea-weed, the latter is carbonized in retorts and sodium iodide is extracted with water from the residue. This is then treated with manganese dioxide and sulphuric acid. The quantity of manganese dioxide is carefully measured so as to be just sufficient to set free the iodine contained in the liquid, without proceeding farther to the liberation of the chlorine which it contains in much larger amounts. When the mixture is heated, the iodine passes off in the form of vapor, and is condensed in a suitable receiver. The action (*cf.* pp. 157, 194) is:

$$2NaI + MnO_2 + 3H_2SO_4 \rightarrow MnSO_4 + 2NaHSO_4 + 2H_2O + I_2.$$

2. In France the treatment is similar, excepting that chlorine is used to liberate the iodine in the last stage ($2NaI + Cl_2 \rightarrow 2NaCl + I_2$). The quantity is adjusted so that excess may not be employed. The iodine, being insoluble, forms a dense precipitate and, when the liquid is pressed out, it remains behind in the form of a paste.

3. Electricity could also be used for the decomposition of this mother-liquor. The iodine is set free at the positive electrode.

In all cases the iodine is purified by distillation with a little powdered potassium iodide. It condenses in the solid form directly, in glittering, black plates (sublimed iodine). The distillation of a solid body, when a condensation takes place directly to the solid form, is spoken of as *sublimation*.

Physical Properties. — Iodine (Gk., *like a violet*) is a black, solid substance (sp. gr. 5), exhibiting large crystalline plates of rhombic form. It melts at 114°, and boils at 184°. The vapor has at first a reddish-violet tint, and on being more strongly heated becomes deep blue (see next section).

Iodine is very slightly soluble in water (about 1 : 6000), and the solution has a scarcely perceptible brown tint. It is much more soluble in carbon disulphide (p. 12) and in chloroform, in which it gives violet solutions. In alcohol it gives a solution which is brown, the iodine being in a condition of feeble combination, and not simply in solution. An aqueous solution of potassium iodide, hydrogen iodide, or any other iodide, has likewise the power to take up large quantities of iodine. Here the formation of definite compounds (such as, $KI + I_2 \rightleftarrows KI_3$), by a reversible action, accounts for the amount of iodine taken up.

The behavior of free iodine towards starch forms a distinctive *test* for both substances (*cf.* p. 3). The pale-brown aqueous solution, for example, when added to starch emulsion, produces a deep-blue color. This blue substance is not a chemical compound. The iodine is adsorbed by the starch, which is in colloidal suspension (*q.v.*).

Chemical Properties. — The molecular weight of iodine, ascertained by weighing the vapor at temperatures from the boiling-point up to 700°, is 253.8. The atomic weight being 126.92, the molecule contains two atoms. Beyond 700°, the vapor diminishes in density more rapidly than Charles' law would lead us to expect, and at 1700° the molecular weight has fallen to 127 (*cf.* p. 117). As the vapor is heated, a larger and larger proportion of the molecules is broken up, until the decomposition has become complete. As in all cases of dissociation, when the vapor is cooled the atoms recombine to form molecules. This is the most notable case in which we encounter both the monatomic and the diatomic forms of the same element. The heat given out when the atoms reunite to form the molecules is very considerable ($2I \rightleftarrows I_2 + 28{,}500$ cal.), indicating that the chemical union of two atoms of identical nature may be as vigorous as that of two atoms of different chemical substances. The heat of union of atomic hydrogen (p. 113) is even greater ($2H \rightleftarrows H_2 + 90{,}000$ cal.). In both cases, in accordance with Van't Hoff's law (p. 189), raising the temperature increases the dissociation, because that is the direction in which heat is absorbed.

Iodine *unites* very slowly with hydrogen, even when heated. It unites directly with some non-metals and with the majority of the metals. When phosphorus is presented in the yellow form, the action takes place spontaneously without the assistance of heat. Both chlorine and bromine *displace* iodine from combination with hydrogen and the metals ($2HI + Br_2 \rightarrow 2HBr + I_2$).

The action may be brought about either with the substances in dry form or with their aqueous solutions.

Iodine and its compounds are much **used** in the arts and medicine. Iodine is applied, in the form of an alcoholic solution (tincture of iodine), for the reduction of some swellings. It is required in making iodoform CHI_3, and the iodides of potassium, rubidium, and sodium, which are used in medicine. The emulsion used in making photographic dry-plates contains silver iodide AgI.

HYDROGEN IODIDE HI

Preparation. — The direct union of hydrogen and iodine cannot be employed in preparing pure hydrogen iodide (see below).

The action of concentrated sulphuric acid upon potassium iodide is equally inapplicable. In this case, as in that of hydrogen bromide (p. 196), the sulphuric acid oxidizes the hydrogen halide and much free iodine and hydrogen sulphide are formed:

$$H_2SO_4 + 8HI \rightarrow H_2S\uparrow + 4H_2O + 4I_2\uparrow .$$

The action affords a rough **test** for an iodide (*cf.* pp. 3, 200).

Powdered sodium iodide and concentrated phosphoric acid (*cf.* p. 196), when warmed, give pure hydrogen iodide very slowly.

The **best method** is one similar to that described under hydrogen bromide. Phosphorus and iodine unite directly to form PI_3. This is a yellow solid which is violently *hydrolyzed* by water and gives phosphorous acid and hydrogen iodide:

$$PI_3 + 3H_2O \rightarrow P(OH)_3 + 3HI\uparrow .$$

If excess of water, which dissolves hydrogen iodide, is avoided, the latter goes off in a continuous stream in a gaseous condition. The apparatus shown in Fig. 76 may be used. The mixture of iodine and red phosphorus is placed in the flask and the water in the funnel.

Still **another method** of making hydrogen iodide is frequently employed when a solution of the gas in water is required, and not the gas itself. Powdered iodine is suspended in water, and hydrogen sulphide gas (*q.v.*) is introduced through a tube in a continuous stream. The iodine dissolves slowly in the water, I_2 (solid) $\rightleftarrows$ I_2 (dslvd), and acts upon the hydrogen sulphide, which likewise dissolves, H_2S (gas) $\rightleftarrows$ H_2S (dslvd). Sulphur separates in a fine powder, S (dslvd) $\rightleftarrows$ S (solid), and hydrogen iodide is formed in accordance with the equation:

$$H_2S + I_2 \rightarrow 2HI + S\downarrow.$$

This action takes place, however, only in presence of water, although the water does not appear in the equation. The solution is freed from the deposit of sulphur by filtration, and may be concentrated to 57 per cent of hydriodic acid by distilling off the water.

Physical Properties. — Hydrogen iodide is a colorless gas with a sharp odor. Its molecular weight is 128, and it is therefore much heavier than air, the average weight of whose molecules is 28.955 (p. 101). It is a nonconductor of electricity, both in the gaseous and in the liquefied conditions. It is exceedingly soluble in water, so that at 10° 30 grams of water will absorb 70 grams of the gas, giving a 70 per cent solution (425 vols. : 1 aq). The behavior of this solution is similar to that of hydrogen chloride and hydrogen bromide (*cf.* p. 145). The mixture of constant boiling-point distils over at 127° (at 760 mm.), and contains 57 per cent of hydrogen iodide.

Chemical Properties. — Hydrogen iodide is the least stable of the hydrogen halides. When heated it begins visibly to decompose into its constituents at 180°. On account of the ease with which it parts with the hydrogen which it contains, it can be burned in oxygen gas, $4HI + O_2 \rightarrow 2H_2O + 2I_2$. When the gas is mixed with chlorine, a violent chemical change, accompanied by a flash of light, occurs, the iodine is set free, and hydrogen chloride is produced, $Cl_2 + 2HI \rightarrow 2HCl + I_2$. Bromine vapor will similarly displace the iodine from hydrogen iodide.

Chemical Properties of Hydriodic Acid HI, Aq. — In most respects the aqueous solution behaves exactly like hydrochloric and hydrobromic acids. With oxidizing agents, for example, such as manganese dioxide, it gives free iodine, just as the others (p. 158) give free chlorine and bromine, respectively. Here, however, the oxidation is so much more easily carried out, that it is slowly effected by atmospheric oxygen, so that hydriodic acid left exposed to the air gradually becomes brown ($O_2 + 4HI \rightarrow 2H_2O + 2I_2$).

Although the dry gas is not an acid, the solution has all the ordinary properties of this class of substances (*cf.* p. 52). The hydrogen may be displaced by metals like zinc and magnesium (p. 60). The acid interacts with oxides and hydroxides, forming iodides and water (p. 146).

The Direct Union of Hydrogen and Iodine. — The union of hydrogen and iodine, giving hydrogen iodide, is a reversible reaction:

$$2HI \rightleftarrows H_2 + I_2.$$

That is to say, whether we charge a tube with hydrogen iodide, or with an equal amount of the elements in the correct proportions by weight, if we place *both* tubes in a bath, and keep them thus at the same temperature, the contents of the tubes will after a time be *identical* (p. 177). At 283°, there will be 82 per cent of the compound, and 18 per cent of the uncombined elements. At 508° the proportions will be 76 per cent and 24 per cent, respectively.

The proportion of the elements increases with rise in temperature because the dissociation absorbs heat (p. 189).

At any one temperature, say 283°, the equilibrium point can be **displaced in either direction** (p. 181). If we introduce some additional hydrogen (or iodine), without enlarging the tube, thus increasing the concentration of the hydrogen (or iodine), *more* than 82 per cent of the compound is formed. If, instead, we let one end of the tube project, and cool this end, the iodine condenses to solid form, while the other two substances remain gaseous. This lowers the concentration of the iodine in the gaseous mixture, and lowers the speed and force of the union of the elements. It does not affect the tendency to dissociation of the compound molecules, but, since it interferes with the formation of more of them, it enables the dissociation to proceed to practical completion. The condensation of the iodine is essentially like a precipitation (pp. 144, 186).

This reaction illustrates very clearly the way in which the progress of a reversible, chemical action is controlled by mechanical causes. It shows also why we do not prepare the compound by uniting the elements: (1) Since the elements interact as gases, very bulky apparatus would be required to prepare any considerable quantity; (2) the union is very slow, taking many hours at 283°; (3) it is incomplete, at best, and we obtain a mixture, and not a pure substance.

Note that, removing one product is, in general, more effective than increasing the concentration of one of the interacting substances. The concentration of one product can be reduced to zero. To achieve the same effect by *adding* an interacting substance, the concentration of the latter would have to be raised to infinity, which is impossible.

FLUORINE F_2.

The discussion of this element should logically have preceded that of chlorine, since it is, of all the members of the halogen family, the most active. Chlorine was taken up first, however, because its compounds are more familiar. Fluorine is found in nature chiefly in the mineral **fluorite,** calcium fluoride CaF_2 and in **cryolite,** a double fluoride of aluminium and sodium $3NaF, AlF_3$.

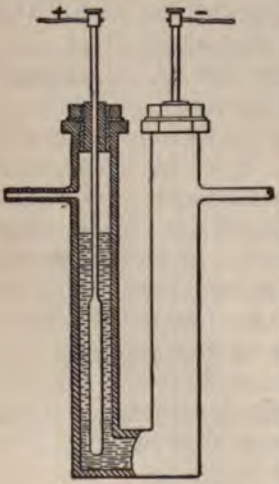


Fig. 77.

Preparation. — When a solution of hydrofluoric acid is heated with manganese dioxide, oxidation does not occur and free fluorine is not produced. Until recently all efforts to isolate the element failed. It was perfectly understood that the reason of these failures lay in the greater chemical activity of fluorine, which made it more difficult of separation from any state of combination than the other halogens. Its preparation was finally achieved by Moissan (1886) by the decomposition of anhydrous hydrogen fluoride, which is liquid below 19°, by means of electricity. The apparatus (Fig. 77) is made of copper, which, after receiving a thin coating of the fluoride, is not further affected. To reduce the tendency to chemical union, the whole is immersed in a bath giving a temperature of − 23°. The electrodes are made of an alloy of platinum and iridium, which is the only material that can resist the action of the fluorine. Hydrogen fluoride, like other hydrogen halides, is a nonconductor of electricity, and a small quantity of potassium-hydrogen fluoride KHF_2 has to be added to enable the current of electricity to pass. The fluorine is set free at the positive electrode, and hydrogen appears at the negative. The U-tube is closed, after the introduction of the hydrogen fluoride, by means of blocks made of calcium fluoride, which is naturally unable further to enter into combination with fluorine. For the reception and examination of the fluorine gas, other copper tubes can be screwed on to the side neck of the apparatus, and, when necessary, small windows of calcium fluoride can be provided.

Physical Properties. — Fluorine is a gas whose color is like that of chlorine, but somewhat paler. Its density (38) shows that the molecule is diatomic (F_2). The gas is the most difficult of the halogens to liquefy. The liquid boils at −186°.

Chemical Properties. — Fluorine unites with every element, with the exception of oxygen, chlorine, nitrogen, and the members of the helium family, and in many cases does so with such vigor that the union begins spontaneously without the assistance of external heat. Dry platinum and gold are the elements least affected. It explodes with hydrogen at the ordinary temperature, without the assistance of sunlight. On the introduction of a drop of water into a tube of fluorine, the oxygen of the water (vapor) is instantly *displaced* by fluorine, and the vessel is filled with the deep-blue gas, ozone: $3F_2 + 3H_2O \rightarrow 3H_2F_2 + O_3$.

Fluorine displaces the chlorine in hydrogen chloride as easily as chlorine in turn displaces bromine or iodine.

HYDROGEN FLUORIDE H_2F_2

Preparation. — Pure, dry hydrogen fluoride is best made by heating potassium-hydrogen fluoride, $2KHF_2 \rightleftarrows K_2F_2 + H_2F_2 \uparrow$. For ordinary purposes, however, the preparation of an aqueous solution is the ultimate object. Usually powdered calcium fluoride is treated with concentrated sulphuric acid, and the mixture distilled in a retort of platinum or lead:

$$CaF_2 + H_2SO_4 \rightleftarrows CaSO_4 + H_2F_2 \uparrow .$$

The hydrofluoric acid passes over and is caught in distilled water. The aqueous solution thus obtained has to be kept in vessels made of lead, rubber, or paraffin, as glass interacts with the acid with great rapidity (see below).

Physical Properties. — Hydrogen fluoride is a colorless liquid, boiling at 19.4°. It mixes freely with water and, on distillation, an acid of constant boiling-point (120° at 760 mm.) containing 35 per cent of hydrogen fluoride is obtained. The weight of 22.4 liters of the vapor varies from 20 g. at 90° and above, to 51 g. at 26°. At 90°, therefore, the formula is HF and at 26° probably a mixture of H_2F_2(40) and H_3F_3(60). Since HF is the only form which persists through a range of temperature, we say this substance shows **association** at lower temperatures. Water is spoken of as an **associated liquid** — the vapor being pure H_2O, but the liquid a mixture of this along with $(H_2O)_2$ and $(H_2O)_3$ (p. 138).

Chemical Properties of Hydrofluoric Acid H_2F_2, Aq. — Metals like zinc and magnesium interact with hydrofluoric acid with evolution of hydrogen (p. 60). The action is less violent than with other halogen acids. The acid interacts with oxides and hydroxides, forming fluorides (p. 146). The chief difference in this respect which it exhibits, when compared with the other halogen acids, is one which leads us to assign to it the formula, H_2F_2. We may displace either *one* or *both* the hydrogen atoms in the molecule with a metal. Thus, one of the commonest salts of hydrofluoric acid is potassium-hydrogen fluoride, or the acid fluoride of potassium KHF_2, mentioned above. In this respect the acid resembles sulphuric acid and other acids containing more than one replaceable hydrogen unit.

The most remarkable property of hydrofluoric acid depends on the great tendency which fluorine has to unite with silicon, forming the gaseous silicon tetrafluoride. Glass (*q.v.*) is essentially a mixture of silicates of calcium and sodium, with excess of silica (sand) SiO_2, and is rapidly decomposed by hydrofluoric acid:

$$CaSiO_3 + 3H_2F_2 \rightarrow SiF_4 \uparrow + CaF_2 + 3H_2O,$$
$$SiO_2 + 2H_2F_2 \rightarrow SiF_4 \uparrow + 2H_2O.$$

In all other silicates, fluorine is *substituted* (p. 162) for oxygen according to the same plan. The silicon tetrafluoride SiF_4 is a gas. The fluorides of calcium and sodium are solid and crumble away or dissolve. Thus the glass is completely disintegrated. The vapor of hydrofluoric acid, generated in the way described above from calcium fluoride in a lead dish, is used for etching glass. The surface of the glass is covered with paraffin to protect it from the action of the vapor, and with a sharp instrument portions of this paraffin are removed where the etching effect is desired. The vapor gives a rough surface where it encounters the glass (**test** for a fluoride). In this way, the graduation on thermometers, burettes, and other pieces of apparatus, is marked. The aqueous solution makes smooth depressions on the surface of glass. It is **used** for removing sand from metal castings and for cleaning the exteriors of buildings of granite and sandstone.

THE HALOGENS AS A FAMILY

The most noticeable fact is that, if we **arrange the halogens in order in respect to any one property,** chemical or physical, **the other properties will be found to place them in the same order.** In the table, the sixth column contains the weight of the element dissolving in 100 c.c. of water (15°). The last column, cal. K*X*, gives the heat of formation of one gram-molecule of the potassium halide.

Element.	Atomic Weight.	State.	Boiling-point.	Color.	Solubility.	Cal. K*X*.
Fluorine . .	19.0	gas	−187°	yellow	....	118,100
Chlorine . .	35.5	gas	− 34°	yellow	7.2	104,300
Bromine . .	79.9	liquid	+ 59°	brown	3.2	95,100
Iodine . . .	126.9	solid	184°	violet	0.015	80,100

It will be seen that, as the atomic weight increases, the boiling point (b.-p.) rises, the color deepens, the solubility diminishes, and the heat of union with potassium becomes smaller. The vigor with which the halogens unite with hydrogen and the metals is greatest with fluorine and diminishes progressively until we reach iodine. We shall see later that the affinity for oxygen, on the other hand, *increases* as we pass from fluorine to iodine.

Although showing different degrees of activity, the halogens are closely alike in chemical nature. That is, the **relations** (p. 163) they show when in combination are similar. When united with hydrogen and the metals, they are all *univalent*. In their oxygen compounds, however, they exhibit a higher valence. Their oxides interact with water to give acids, and they are therefore non-metals (p. 94). They are strongly electro-negative (pp. 55, 194), as non-metals all are. Their hydrides, when dissolved in water, are all active acids. This, and their valence, distinguish the halogen family from other groups of non-metals. Thus, oxygen and sulphur are bivalent (and the latter sexivalent also), and the hydrides of oxygen (H_2O and H_2O_2) and of sulphur (H_2S) are very feeble acids.

Order of Activity of the Non-Metals. — The way in which chlorine displaces bromine and iodine from bromides (p. 194) and iodides (p. 199), and bromine, in turn, displaces iodine suggests an order of activity for non-metals. It was noted that oxygen displaces iodine from hydriodic acid (p. 202) and that iodine displaces sulphur from hydrogen sulphide (and all other sulphides). The order is, therefore, F, Cl, Br, O, I, S.

Compounds of the Halogens with Each Other

Iodine unites directly with chlorine to form two compounds. The more familiar one is a red crystalline substance, **iodine monochloride** ICl. Another compound, ICl_3, is made by the use of excess of chlorine. Iodine unites with bromine to form the compound IBr, while a compound with fluorine, IF_5 is supposed to exist. None of these compounds are particularly stable, and some of them decompose easily.

Exercises. — 1. What impurities is commercial iodine likely to contain? In what way does heating with potassium iodide (p. 199) free it from these?

2. Classify all the chemical actions in this chapter according as they belong to one or other of the ten kinds (p. 166).

3. What are the relative volumes of the gases in the interaction of chlorine with hydrogen bromide (p. 198), and hydrogen iodide (p. 202), respectively?

4. Tabulate, more fully and specifically than is done in the section on "The Halogens as a Family," (*a*) the physical properties, (*b*) the chemical properties, (*c*) the chemical relations, of the members of this group.

5. Construct the equation on p. 199 by the use of partial equations as in the example on p. 195.

6. What are the relative volumes of fluorine and ozone in the action of the former upon water (p. 205)?

7. What relative volumes of chlorine and iodine vapor must be taken to make the two chlorides of iodine (p. 208), respectively?

8. At a given temperature, would increasing the pressure in a mixture of hydrogen and bromine vapor render the union more or less complete? Is the action more complete at a high or at a low temperature?

CHAPTER XVI

DISSOCIATION IN SOLUTION

THE employment of interacting substances in the form of solutions is so constant in chemistry, and the reasons for this are so cogent, that we must now resume the discussion of this subject (*cf.* p. 121).

The present chapter will be devoted to giving the proofs that the molecules of **acids, bases, and salts,** in aqueous solutions, are **actually dissociated into parts** by the solvent. This will be shown by consideration, successively, of certain peculiarities in the **chemical behavior,** in the **freezing-points** and in the **boiling-points** of the solutions of these substances. We shall see that **these parts coincide in composition with the radicals.**

Some Characteristic Properties of Acids, Bases, and Salts, Shown in Aqueous Solution. — **Acids all** contain hydrogen (p. 53). In aqueous solution, if soluble, they are sour in taste, they turn blue litmus red, and their hydrogen is displaced by certain metals (p. 53), and has the properties of a radical. By the last statement is meant that it very readily exchanges places with other radicals in reversible double decompositions (p. 147). Amongst the acids mentioned have been: hydrochloric acid HCl, sulphuric acid H_2SO_4, hypochlorous acid $HClO$, acetic acid HCO_2CH_3. Many other bodies, like sugar, kerosene, and alcohol, contain hydrogen also, but not one of them shows all of these properties.

Again, **all salts** are made up of two radicals, and the reversible double decompositions into which they enter with acids, bases, and other salts, consist in exchanges of these radicals. Other substances may include the same combinations of atoms, but in their actions these groupings are often disregarded. Thus, sodium chloride $NaCl$ and silver nitrate $AgNO_3$ exchange radicals completely (p. 147) and, in dilute solution, hydrogen chloride and sodium-hydrogen sulphate do so partially (p. 143). But sodium chloride and nitroglycerine $C_3H_5(NO_3)_3$ do not interact at all. The latter is not a salt, although it contains the same proportion of nitrogen to oxygen as does any nitrate.

All **bases** contain hydroxyl OH as a radical, combined with some positive radical. Potassium hydroxide KOH is soluble and active, zinc hydroxide $Zn(OH)_2$ and many others, however, are insoluble. Bases all exchange radicals readily in double decomposition with salts and acids. Other substances, like alcohol C_2H_5OH, may contain hydroxyl, but do not interact readily with salts like NaCl, and are not bases.

The Influence of Water and Other Solvents. — It is chiefly **in aqueous solution** that these special properties of acids, bases, and salts become apparent. Their behavior is often quite different in the absence of this solvent. If, for example, we mix together **dry** ammonium carbonate $(NH_4)_2CO_3$ and partially dehydrated, solid cupric nitrate $Cu(NO_3)_2$, and apply heat, a violent interaction begins. An immense cloud of smoke and gas is thrown out of the tube, and the substance remaining is either black, or reddish, in parts, according to the proportions of the substances employed. The residue contains cupric oxide, and sometimes red cuprous oxide Cu_2O. The gas is tinged red by the presence of nitrogen tetroxide NO_2, while a more careful examination would show that it contained carbon dioxide, nitrogen, nitrous oxide N_2O, water vapor, and perhaps still other products.

The **contrast,** when these substances are **dissolved in water** before being brought in contact with one another, is very great. A pale-green precipitate is formed at once, and rapidly settles out. On examination, this turns out to be a carbonate of copper (basic), while evaporation of the solution furnishes us with ammonium nitrate. There are only two main products, and the essential part of the action in solution may be represented by the equation:

$$(NH_4)_2CO_3 + Cu(NO_3)_2 \rightarrow CuCO_3\downarrow + 2NH_4NO_3.$$

In the interaction between the *dry* substances the molecules are completely disintegrated, the whole change is very complex, and it takes a good deal of time. In the action in water no heating is required, the substances are neatly broken apart, certain groups of atoms, which we call radicals, are transferred as wholes from one state of combination to another, and the rearrangement takes place instantaneously in a machine-like manner. Contrasts like this between the interactions of anhydrous and dissolved bodies are very common.

Many compounds, however, do not show any change in behavior when dissolved in water. Sugar, for example, is, as a rule, more readily acted upon in the absence of any solvent. Then again, while **water** is not the only solvent which has the effect we have just described, the majority of solvents, if they affect chemical change at all, simply retard it. Thus the union of iodine and phosphorus in the absence of a solvent takes place spontaneously with a violent evolution of heat. When the elements are dissolved in carbon bisulphide, before being mixed, the action is much milder, although the product is the same (phosphorus tri-iodide). The diminution in the concentration of the ingredients has decreased the speed of the action in the normal way (p. 181). That water and some other solvents have a specific influence tending to increase the apparent activity of certain classes of substances, shows that a special explanation of the phenomenon must be found.

Summing up these points we see that the peculiarity of acids, bases, and salts *in aqueous solution* is that the action is complete as soon as the solutions have been mixed, and that each compound always splits in the same way. Thus, cupric nitrate always gives changes involving Cu and NO_3 and never interacts so as to use CuN_2 and O_3, or CuO_2 and NO_2, as the basis of exchange. Similarly, *dilute* acids always offer hydrogen in exchange, and so nitric acid behaves as if composed of H and NO_3, and sulphuric acid as if composed of 2H and SO_4, and never as if made up of HSO and HO_3, or H_2S and O_4. The sour taste and the effect upon litmus seem to be properties of this easily separable hydrogen, for they are shown only by acids. The result is that we can make a list of the units of exchange, such as H, OH, NO_3, CO_3, SO_4, Cu, K, and Cl, employed by acids, bases, and salts in their interactions. The molecule of each compound of these classes contains at least two of them. Even when these units contain more than one atom, their coherence is as noticeable within this class of actions, as is the permanence of the atomic masses themselves in all actions.

The question raised in our minds is whether solution in water alters the character of the molecule, simply by producing a sort of *plane of cleavage* in it which creates a predisposition to a uniform kind of chemical change, or whether it *actually divides* the molecules into separate parts consisting of the above units of exchange, and leaves subsequent chemical actions to occur by cross-combination of these fragments. The fact that the dissolved substances can be recovered by evaporation of the liquid does not demonstrate that they have not been decomposed temporarily while in solution. The alteration which the water produces, whatever it be, will naturally be reversed when the water is removed. Since our question involves nothing but the counting of particles, the number of which would be much greater in the event that actual subdivision of molecules is the explanation, it can be answered by a study of the physical properties of solutions. Several physical properties can be used, and they give concordant answers to the question. We shall confine ourselves here, however, mainly to the evidence furnished by the freezing-points and boiling-points of solutions.

Laws of Freezing-Point Depression. — Every pure liquid has a definite temperature at which it freezes. Thus, pure water freezes at 0° and benzene at 5.48°. As we have seen (p. 134), however, the presence of a foreign, dissolved body lowers the freezing-point, although the "ice" which separates usually consists of crystals of the pure solvent only.

The depression in the freezing-point is directly proportional to the weight of dissolved substance in a given amount of the solvent. The depression is inversely proportional to the amount of solvent. Thus, if we double the concentration of the solution, the depression in the freezing-point is doubled. Thus, in one set of experiments, solutions of sugar containing 11.4 g., 22.8 g., and 34.2 g. of sugar to 100 g. of water were found to freeze at $-0.62°$, $-1.24°$, and $-1.86°$, respectively.

Further, **equal numbers of molecules of different solutes in the same quantity of solvent give equal depressions.** Or, in other words, the depression is proportional to the concentration of the molecules of the solute. Thus, solutions containing 342 g. of sugar $C_{12}H_{22}O_{11}$,* or 46 g. of alcohol C_2H_6O, or 74 g. of methyl acetate $CH_3(C_2H_3O_2)$, in 1000 g. of water being weights which contain equal numbers of molecules show a depression below the freezing-point of water of about 1.86° in each case. That is, such solutions all freeze close to −1.86°. This depression, produced by a mole of the solute in 1000 g. of solvent, is called the molecular depression constant, and has a different value for each solvent. For solutions of the same molecular concentration in benzene the depression is 5.1°, in phenol (carbolic acid) 7.3°. Combining these facts in one expression:

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* $12 \times 12 + 22 \times 1 + 11 \times 16 = 342$.

$$\left(\begin{array}{c}\text{The observed depression}\\ \text{in an aqueous solution}\end{array}\right) = 1.86° \times \frac{\text{Wt. of Solute}}{\text{Mol. Wt. of Solute}} \times \frac{1000}{\text{Wt. of Solvent}}$$

For other solvents, the corresponding value of the depression constant must be substituted for 1.86°.

These laws describe the facts most exactly when the solutions are dilute. They hold only when there is no chemical interaction between solute and solvent. Even so, however, acids, bases, and salts dissolved in water present many apparent exceptions and must be discussed separately (see below).

It will be noted that, when the other factors in the foregoing equation are known or observed, the molecular weight of the solute may be determined. This fact makes possible the determination of this constant for substances which are not volatile (see Hydrogen peroxide).

Abnormal Freezing-Point Depression: Dissociation in Solution. The substances which present the most conspicuous exceptions to the above rules are acids, bases, and salts in aqueous solution. With most of these, the depression produced is abnormal; it is greater than we should expect from the concentration of the solution. Thus, in an actual experiment, two equi-molar solutions were compared. One contained one mole (74 g.) of methyl acetate, and the other one mole (58.5 g.) of sodium chloride, each dissolved in 2000 g. (2 liters) of water. The freezing-points observed were:

Pure water	0.000°	Pure water	0.000°
Sol. of methyl acetate .	−0.970°	Solution of salt	−1.678°
Depression	0.970°	Depression	1.678°
			0.970°
		Excess depression by salt	0.708°

The solution of methyl acetate, as it contained only 0.5 moles of the solute per liter of water, showed, as it should do, about half the average molecular depression (1.86°, p. 214). This is typical of the class of substances showing normal behavior. Sugar, alcohol, and hundreds of other substances, in solutions of the same molar concentration, would have given the same value.

The freezing-point of the salt solution, however, was much lower. If this solution had really contained the same concentration of dissolved molecules as the other solution, its depression would likewise have been 0.970°. The number of molecules in the solution must therefore have been greater than we should have expected from the number of molecules taken. In other words, a portion of the molecules of the salt must have been broken up, and the excess depression, 0.708°, must have been due to the *extra molecules produced by dissociation.* Now sodium chloride molecules cannot give more than two particles each, and the depression is proportional to the number of particles. It follows, therefore, that $\frac{708}{970}$, or 0.732 (73.2 per cent) of the molecules were dissociated:

$$(27 \text{ per cent}) \ NaCl \rightleftarrows (Na) + (Cl) \ (73 \text{ per cent}).$$

This result is typical also. Acids, bases, and salts, of which one mole is dissolved in two liters of water, are found to give irregular values, all more or less in excess of 0.970°. Those which contain but two radicals, like sodium chloride NaCl and potassium nitrate KNO_3, give values between 0.970° and 2 × 0.970°. Substances like calcium chloride $Ca(Cl)_2$ and sodium sulphate $(Na)_2SO_4$ give depressions approaching three times the normal value: their molecules contain three radicals. The excess depression depends, therefore, upon the number of particles which each molecule can furnish, and upon the proportion of all the molecules which is dissociated into these fragments.

In the case of an acid, base, or salt, the depression is not strictly proportional to the concentration. Thus, one mole of salt in *four* liters of water does not give half the depression of the two-liter solution ($1.678° \div 2 = 0.839°$) but *somewhat more* (about 0.844°). The same method of calculation indicates, therefore, a greater degree of dissociation (about 79 per cent) in the more dilute solution (see Ionic equilibrium).

Acids, bases, and salts, so far as they are soluble in materials like toluene, benzene, chloroform, and carbon bisulphide, exhibit simply normal depressions in these solvents. It appears, therefore, that, in many solvents, dissociation does not take place. In common experience it is encountered only in solutions in water, and in alcohol.

Abnormal Boiling-Point Elevation. — We have seen (p. 135) that 342 g. of sugar, or an equal number of molecules of glycerine $C_3H_8O_3$ (92 g.), dissolved in 1000 c.c. of water, will elevate the boiling point from 100° to 100.52°. One molecular weight of sodium chloride (58.5 g.), however, will elevate the boiling-point of the water 0.87° instead of 0.52°. The effect is 0.35°, or 67 per cent greater, indicating dissociation of this proportion of the NaCl molecules. In more dilute solutions, the elevation is relatively greater. Salts containing more than two radicals, like $Ca(Cl)_2$, give elevations of more than twice the normal value. In solvents like benzene and carbon disulphide, however, no abnormal elevation is observed with any solute. The phenomena are, in fact, parallel with those connected with the freezing-point.

Other Evidence of Dissociation. — The freezing-point and boiling-point are only two of *four* properties of solutions which can be used for determining the numbers of molecules present. Numerous measurements show that aqueous solutions of acids, bases, and salts have also abnormal osmotic pressures (*cf.* p. 135). The electrical conductivity is the fourth property which gives the required information (see Chap. XVIII). Now, when we observe the behavior of the same solution in each of these four ways, and calculate the degree of dissociation from the result of each measurement, we find that the values obtained are usually identical, within the limits of error to which the methods are liable. Thus the indications of dissociation found in the chemical behavior of acids, bases, and salts (pp. 211–213) are fully confirmed by a study of the physical properties of their solutions.

Applications: The Constitution of Solutions of Acids, Bases, and Salts. — The composition of solutions which are normal or abnormal, in respect to osmotic pressure, freezing-point, and boiling-point, may be shown thus:

Solutes.	Dissolved in Water, Alcohol, etc.	Dissolved in Toluene, Chloroform, etc.
Acids, bases, salts	Abnormal	Normal
Other substances	Normal	Normal

It appears that water and some other solvents have the power of decomposing acids, bases, and salts. Such solvents have, in fact, an effect on these materials that resembles, outwardly at least, the effect which heat has on many substances (*e.g.*, p. 117), **they cause dissociation:**

$$CaCl_2 \rightleftarrows (Ca) + 2(Cl).$$

In consequence of this, our view of the nature of an aqueous solution of hydrogen chloride HCl, or common salt $NaCl$, or sodium hydroxide $NaOH$, or any of the substances of the classes which these represent, may now be stated in definite terms. Such a solution contains, besides undivided molecules of the solute, at least two other kinds of material, H, Na,* Cl, OH, etc., which result from the breaking up of the molecules. We shall see that these subdivisions of the original molecules have distinct physical and chemical properties of their own. The descriptions of the "properties" of the solutions, as they used to be given in chemistry, were really a confused statement of the properties of the different components of a mixture.

The *free* radicals, of whose existence we have thus become convinced, constitute a new set of materials (with appropriate names. See p. 236). Thus the hydrogen radical of acids, although a form of uncombined hydrogen, differs totally from the gas which is composed of the same material. The gas has no sour taste or effect upon litmus; these are properties of the free radical. The gas is very slightly soluble in water, while the hydrogen radical exists as a separate substance only in solution. Again, substances with the composition of the radicals NO_3 and SO_4 are not known at all except in solutions.

Exercises. — 1. What depression in the f.-p. of water will be produced by dissolving 10 g. of bromine in 1 kg. of this solvent?

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* The objection that separate atoms of sodium could not remain free in water, will be disposed of later.

2. What depressions in the f.-p. of benzene and of phenol would be produced by 10 g. of bromine to 1 kg. of the solvent, if no chemical action took place?

3. What is the molecular depression-constant of a solvent in which 5 g. of iodine in 500 g. of the solvent lowers the f.-p. 0.7°?

4. What is the degree of dissociation of zinc sulphate, if 5 g. of it dissolved in 125 g. of water produce a lowering of 0.603° in the f.-p.?

5. In a decinormal solution, potassium chloride is 86 per cent ionized. What is the freezing point of this solution?

CHAPTER XVII

OZONE AND HYDROGEN PEROXIDE

A FRESH, penetrating odor, resembling that of very dilute chlorine, was noticed by van Marum (1785) near an electrical machine in operation. Schönbein (1840) showed that the odor was that of a distinct substance, which he named ozone (Gk., *to smell*), and he discovered a number of ways of obtaining it. It is very questionable whether there is any ozone in the air, excepting temporarily in the immediate neighborhood of a natural or artificial discharge of electricity.

Preparation of Ozone O_3. — The most satisfactory way of preparing ozone is to allow electric waves to pass through oxygen. The apparatus (Fig. 78) consists of two co-axial glass tubes, between which the oxygen flows. The waves are generated by connecting an outer layer of tinfoil on the outer tube, and an inner layer of tinfoil in the inner tube with the poles of an induction coil. With dry, cold oxygen, about 7.5 per cent of the gas is turned into ozone.

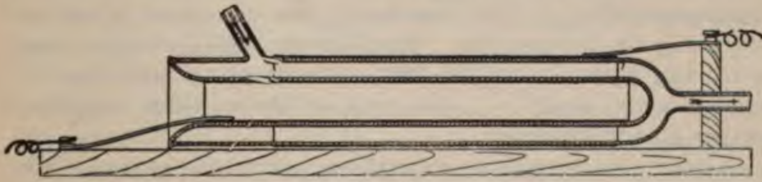

FIG. 78.

Ozone is found in the oxygen generated by electrolysis of dilute sulphuric acid (p. 55). It arises during the slow oxidation of phosphorus by the air, resulting, probably, from the decomposition of unstable, highly oxidized bodies which are formed during the action. Oxygen containing 15 per cent of it is produced by the interaction of fluorine and water (p. 205). Ozone is formed also when a jet of burning hydrogen, or an electrically heated loop of platinum wire is immersed in liquid oxygen. This method shows that ozone is formed at high temperatures, and survives when cooled suddenly by the liquid oxygen.

Physical Properties of Ozone. — Ozone is a gas of blue color. It boils at $-119°$, so that when a mixture of oxygen and ozone is led through a U-tube immersed in liquid oxygen ($-182.5°$), the ozone collects in the tube as a deep-blue fluid. Ozone is much more soluble in water than is oxygen. At 12°, 100 volumes of water would dissolve 50 volumes of the gas at one atmosphere pressure.

Chemical Properties of Ozone. — The density of ozone is one-half greater than that of oxygen. Its molecular weight is therefore 48, and its formula O_3. Being formed with absorption of energy, ozone is most stable at very high temperatures (Van't Hoff's law, p. 188).

$$3O_2 + 61{,}400 \text{ cal.} \rightleftarrows 2O_3.$$

When produced in cold oxygen, by energy from electric waves, it decomposes slowly. But this change, like all others, is hastened by raising the temperature. Equilibrium, with almost no ozone, is reached instantly at 250–300°. Liquid ozone sometimes decomposes explosively. As the equation shows, three volumes of oxygen give two of ozone.

Ozone is a much more active oxidizing agent than oxygen. Mercury and silver, which are not affected by the latter, are converted into oxides by the former. Silver gives the peroxide, Ag_2O_2, thus:

$$2Ag + 2O_3 \rightarrow Ag_2O_2 + 2O_2.$$

Paper dipped in starch emulsion containing a little potassium iodide is used as a **test** for ozone:

$$O_3 + 2KI + H_2O \rightarrow O_2 + 2KOH + I_2.$$

The iodine gives a deep-blue color to the starch (*cf.* p. 200). This test, however, will not distinguish ozone from chlorine or hydrogen peroxide, and may, therefore, be used only in the absence of these substances.

Ozone also removes the color from many of the vegetable coloring matters and artificial dyes. It should be understood that the great majority of the complex compounds of carbon are colorless. Even a slight chemical change, affecting only one or two of the atoms in a complex molecule, is thus almost sure to give a colorless or much less strongly colored material. **Indigo,** $C_{16}H_{10}N_2O_2$, which has a deep-blue color, is an example of a vegetable dye that is also made artificially. When ozonized air is bubbled through a dilute solution of this dye (as indigo-carmine), the indigo is oxidized to isatin $C_8H_5NO_2$, and the color disappears (see below).

Ozone is used commercially in bleaching oils, waxes, ivory, flour, and starch. It is employed also for sterilizing drinking water in Petrograd, Lille, and other cities. For this purpose, however, bleaching powder is less expensive.

Oxidizing Agents, and Explanation of their Activity. — When ozone turns into oxygen much heat is liberated (equation, above). Ozone possesses, therefore, much more internal energy than does oxygen. On this account it brings to the task of oxidizing any substance more energy than does oxygen itself, and is therefore more efficient. Thus, free oxygen does not interact in the cold with indigo, or with silver or potassium iodide (see above), while ozone oxidizes them rapidly.

The heats of reaction show the difference very clearly. In equation (2), 1800 cal. is the amount of heat which would be liberated if indigo could be oxidized to isatin by oxygen gas. When ozone is used, we obtain, *in addition*, the heat of decomposition of this substance (equation 1), so that the total heat liberated (equation 3), 63,200 cal., is 35 times as great as in equation (2) where free oxygen is the oxidizing agent:

$$\begin{array}{rcll} 2O_3 & = & 2O_2\,(+\,2O) \quad + & 61{,}400 \text{ cal.} \quad (1) \\ C_{16}H_{10}N_2O_2 + (2O) & = & 2C_8H_5NO_2 \quad + & 1800 \text{ cal.} \quad (2) \\ \hline C_{16}H_{10}N_2O_2 + 2O_3 & = & 2C_8H_5NO_2 + 2O_2 + & 63{,}200 \text{ cal.} \quad (3) \end{array}$$

By similar reasoning we explain the superiority of potassium permanganate over free oxygen for oxidizing hydrochloric acid (p. 157). Substances which are more active oxidizers than is free oxygen may be called active oxidizing **agents.**

It should be noted that when ozone acts as an oxidizing agent, usually only one of the atoms of oxygen in each molecule plays this part, and oxygen gas is formed. This is illustrated in all the three examples cited in the preceding section.

Allotropic Modifications. — We have seen that a substance may exist in more than the three regular states, solid, liquid, and gaseous. When a simple substance shows more than one form, in the same state, like oxygen and ozone, we call them **allotropic modifications.**

HYDROGEN PEROXIDE H_2O_2

Hydrogen peroxide is found in minute amounts in rain and snow. It is formed in small quantities, in a way not at present fully understood, when moist metals, like zinc, lead, and copper, rust.

Preparation of Hydrogen Peroxide. — When sodium peroxide is added, a little at a time, to a cold dilute acid, hydrogen peroxide is set free and remains dissolved in the liquid.

$$Na_2O_2 + 2HCl \leftrightarrows 2NaCl + H_2O_2.$$

When hydrated barium peroxide ($BaO_2,8H_2O$) is shaken with cold, dilute sulphuric acid a similar action takes place:

$$BaO_2 + H_2SO_4 \leftrightarrows BaSO_4\downarrow + H_2O_2.$$

Phosphoric acid is largely employed instead of sulphuric acid in the commercial manufacture of hydrogen peroxide, and great care is taken to precipitate the other products and all impurities from the solution.

An aqueous solution is also obtained by passing carbon dioxide through barium peroxide suspended in water:

$$BaO_2 + CO_2 + H_2O \leftrightarrows BaCO_3\downarrow + H_2O_2.$$

Pure hydrogen peroxide is isolated from any of these solutions by distillation under reduced pressure. To secure the low pressure, the ordinary distilling apparatus (Fig. 51, p. 93) is made completely air-tight, and is connected by a branch tube with a water-pump. Hydrogen peroxide is much less volatile than water, but decomposes into water and oxygen violently at 100°. Hence the lower pressure is required to make possible its volatilization at a temperature below this point. At 26 mm. pressure, the water begins to pass off first (at about 27°). The last portion of the liquid boils at 69° and is hydrogen peroxide.

By evaporating the commercial (3 per cent) solution at 70°, a liquid containing 45 per cent of hydrogen peroxide may be made without much loss of the material by volatilization.

Physical Properties. — Hydrogen peroxide (100%) is a syrupy liquid of sp. gr. 1.5. It blisters the skin and, when diluted, has a disagreeable metallic taste. It has been frozen (m.-p. $-2°$).

Chemical Properties. — Hydrogen peroxide (100 per cent) is very **unstable,** and decomposes slowly even at $-20°$. The dilute aqueous solution, when free from impurities, keeps fairly well. The presence of a trace of free acid increases its stability. Free alkalies and most salts assist the decomposition; hence the necessity for purifying the commercial solution. Addition of powdered metals, of manganese dioxide, or of charcoal (contact action) causes effervescence even in dilute solutions, and oxygen escapes:

$$2H_2O_2 \rightarrow 2H_2O + O_2.$$

Since the substance cannot be vaporized, even at low pressure, without some decomposition, its molar weight has been determined by the freezing-point method. The freezing-point of a 3.3 per cent solution in water was $-2.03°$. Substitution of these data in the formula (p. 214) gives 31.8 g. as the **molar weight.** Now the formula HO corresponds to a molar weight of 17 and H_2O_2 to one of 34. It is evident, therefore, that the latter is the correct formula.

Hydrogen peroxide, in solution in water, is a **feeble acid.** As an acid it enters into double decomposition readily, and the peroxides are salts with the negative radical O_2^{II} (peroxidates). Thus, when hydrogen peroxide is added to solutions of barium and strontium hydroxides, the hydrated peroxides appear as crystalline precipitates:

$$Sr(OH)_2 + H_2O_2 \rightleftarrows 2H_2O + SrO_2.$$

The precipitation involves another equilibrium: $SrO_2 + 8H_2O \rightleftarrows SrO_2,8H_2O$ (solid).

The formation of a beautiful blue substance by the action of hydrogen peroxide upon dichromic acid is used as a **test.** The test is carried out by adding a drop of potassium dichromate to an *acidulated* solution of the peroxide. The acid interacts with the dichromate, giving free dichromic acid:

$$H_2SO_4 + K_2Cr_2O_7 \rightleftarrows H_2Cr_2O_7 + K_2SO_4.$$

The blue substance, which is very unstable and quickly decomposes, is a perchromic acid. A blue, crystalline perchromic acid $(HO)_4Cr(OOH)_3$, which decomposes above $-30°$, has been prepared. The blue substance has the property, unusual in inorganic compounds, of dissolving much more readily in ether than in water. It is also much less unstable when removed from the foreign materials in the aqueous solution. Hence the test is rendered more delicate by extracting the solution with a small amount of ether. In the ethereal layer the color of the compound is more permanent, as well as more distinctly visible on account of the greater concentration.

Hydrogen peroxide is a much more active **oxidizing agent** than is free oxygen. This would be expected from the fact, that it contains so much more internal energy than the water and oxygen into which it decomposes (p. 223), that 23,100 cal. are liberated in the decomposition of one mole. Thus, it liberates iodine from hydrogen iodide, an action which, in presence of starch emulsion (*cf.* p. 200), is used as a test for its presence:

$$2HI + H_2O_2 \rightarrow 2H_2O + I_2.$$

It converts sulphides into sulphates. The white lead (*q.v.*) used in paintings is changed by the hydrogen sulphide in the air of cities to black lead sulphide: $Pb_3(OH)_2(CO_3)_2 + 3H_2S \rightarrow 3PbS + 4H_2O + 2CO_2$. This may be oxidized to white lead sulphate by means of hydrogen peroxide:

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O,$$

and in this way the original tints of the picture may be practically restored. Organic coloring matters are changed into colorless substances by an action similar to that of ozone (*cf.* p. 221). Hence hydrogen peroxide is used for bleaching silk, feathers, hair, and ivory, which would be destroyed by a more violent agent. The products of its decomposition, being water and oxygen only, are harmless, and, on this account, it is used in disinfecting (destroying organisms in) sores, and as a throat wash.

Hydrogen peroxide exercises the functions of a **reducing agent** in special cases, also. Thus, silver oxide is reduced by it to silver:

$$Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2.$$

A solution of potassium permanganate, in which the permanganic acid has been set free by an acid: $KMnO_4 + H_2SO_4 \rightleftarrows HMnO_4 + KHSO_4$, is rapidly reduced. The permanganic acid, with excess of sulphuric acid, tends to undergo the first of the following changes, *provided a substance*, such as hydrogen peroxide, *is present which can take possession of the oxygen that would remain as a balance:*

$$2HMnO_4 + 2H_2SO_4 \rightarrow 2MnSO_4 + 3H_2O\ (+\ 5O). \qquad (1)$$
$$\underline{(5O) + 5H_2O_2 \rightarrow 5H_2O + 5O_2. \qquad (2)}$$
$$2HMnO_4 + 2H_2SO_4 + 5H_2O_2 \rightarrow 2MnSO_4 + 8H_2O + 5O_2.$$

Exercises. — 1. What volume of ozone will be taken up by 100 c.c. of water at 12° from a stream of oxygen containing 7.5 per cent of ozone (p. 129)?

2. At what temperature will a ten per cent aqueous solution of hydrogen peroxide freeze (p. 214)?

3. Write the thermochemical equations for oxidation of indigo by hydrogen peroxide (pp. 221, 224).

4. How many times its own volume of oxygen gas will a 3 per cent solution of hydrogen peroxide give off when treated with: (*a*) platinum powder (p. 223); (*b*) sulphuric acid and potassium permanganate?

CHAPTER XVIII

IONIZATION

Introductory. — As we have seen, acids, bases, and salts, when dissolved in water, interact with one another by *interchanging radicals* (p. 148). We have also learned that the same solutions have abnormal values for their freezing-points and for two other properties. These facts indicate *dissociation into the radicals* (p. 216). Now precisely these solutions have a property which is not shared by any other solutions, namely, that of being *conductors of electricity and suffering chemical decomposition by the passage of the current.* Such solutions are called, in consequence, **electrolytes,** and the process is named **electrolysis.** Now the natural inference from the foregoing facts is that **the electricity is carried by the liberated radicals.** Our first aim in the present chapter is to show, **by a study of the chemical changes taking place in electrolysis,** that this inference is correct. We then proceed to discuss the **nature of ions** as **a kind of molecules.** Next, we devote ourselves to **the explanation of electrolysis,** to the **equilibrium between the ions and the remaining, undissociated molecules,** and to **conductivity phenomena** as a means of measuring the **fraction ionized.** Finally, we deduce the relation between extent of ionization and **chemical activity.**

Incidentally, the facts to be given provide the means of understanding the electrolytic processes, many of them of great importance in chemical industries, to which frequent reference is made in later chapters.

Non-Electrolytes. — To clear the ground, we should first note the fact that only solutions (as a rule) possess both of the properties in question, namely that of conducting and that of being decomposed by the current. Some substances, notably the metals and materials like carbon, are conductors. But they are not changed chemically by the current. Again, *single* substances, even when they are such as, if mixed, yield electrolytes, are not conductors at ordinary temperatures. Thus hydrogen chloride, whether gaseous or liquefied, is a nonconductor, and water is a very feeble conductor, although the solution of the two conducts exceedingly well. Dry acids, bases, and salts, except when at a high temperature and fused, are likewise nonconductors. Furthermore, even amongst solutions, not all are conductors. Solutions of sugar and other substances of the same class (p. 213), which have normal freezing-points, are nonconductors. Only solutions of acids, bases, and salts in certain specified solvents, of which the commonest is water, are electrolytes at ordinary temperatures.

Chemical Changes Taking Place in Electrolysis: at the Electrodes. — When the wires from a battery are attached to platinum plates immersed in any electrolyte (*e.g.*, Fig. 65, p. 155), we observe that the products appearing at the two electrodes are always different. They may be of several kinds physically, and will be secured for examination variously according to their nature. Thus, when they are **gases,** which are not too soluble, they may be collected in inverted tubes filled with the solution. **Solids,** if insoluble in the liquid, will either remain attached to the electrode or fall to the bottom of the vessel as precipitates. **Soluble substances,** on the other hand, will usually not be visible. They may be handled by interposing a porous partition of some description which will restrain the diffusion of the dissolved body away from the neighborhood of the electrode, while not interfering appreciably with the passage of the current. Surrounding one electrode with a porous battery jar is a convenient method for effecting this.

Of the various illustrations which we have encountered, the electrolysis of hydrochloric acid (p. 155) happens to have been the only one which delivered both components of the solute with a minimum of modification at the electrodes:

$$\text{Neg. Wire, } H_2 \longleftarrow H.Cl \longrightarrow Cl_2\text{, Pos. Wire.}$$

Hydrogen does not interact with water, and chlorine interacts very incompletely, so that the molecular substances H_2 and Cl_2 are promptly formed from the elements H and Cl which are liberated. The chlorides, bromides, and iodides of those metals which do not interact with water (p. 60) give equally simple results:

$$\text{Neg. Wire, } Cu \longleftarrow Cu.Br_2 \longrightarrow Br_2\text{, Pos. Wire.}$$

Thus the solute seems to be *split into its radicals* and, in electrolysis, the radicals, if they do not interact with water, are set free. A substance thus set free is called a **primary product** of the electrolysis. In the foregoing instances both products are primary.

Usually the chemical change is more complex. Thus, when dilute sulphuric acid is electrolyzed, hydrogen and oxygen are liberated at the negative and positive electrodes, respectively. But these products do not account for the whole of the constituents (H_2SO_4). We therefore proceed to examine the materials in solution round the electrodes. It is found that, as the action progresses, sulphuric acid accumulates round the positive wire, while the liquid in the neighborhood of the other pole is gradually depleted of this substance. In view of this fact we easily explain the phenomenon. Evidently the substance divides into its radicals, H and SO_4, but SO_4, not being a known substance, must interact with the water to produce sulphuric acid and oxygen: $2SO_4 + 2H_2O \rightarrow 2H_2SO_4 + O_2$. The whole change may therefore be tabulated as follows:

$$\text{Neg. Wire, } H_2 \longleftarrow H_2.SO_4 \longrightarrow O_2 \text{ and } H_2SO_4\text{, Pos. Wire.}$$

Hence the hydrogen is a primary product, but the oxygen and sulphuric acid are **secondary products.** All acids give hydrogen alone at the negative electrode, whatever may be the product at the positive.

If we electrolyze cupric nitrate solution, we obtain a red deposit of metallic copper on the negative plate and at the positive end oxygen and nitric acid are formed. We infer, therefore, that the division of the original molecule was into Cu and NO_3, but that the latter interacted with the water: $4NO_3 + 2H_2O \longrightarrow 4HNO_3 + O_2$:

$$\text{Neg. Wire, Cu} \longleftarrow \text{Cu}.(NO_3)_2 \longrightarrow O_2 \text{ and } HNO_3\text{, Pos. Wire.}$$

With a solution of potassium chloride we find hydrogen and chlorine appearing at the negative and positive electrodes, respectively. Litmus paper, however, shows the presence in the solution of a base (potassium hydroxide, KOH) at the negative end. We infer that the parts of the parent molecules are K and Cl. The former, since it resembles sodium in being much more active than hydrogen (p. 60), is more difficult to liberate. Hence hydrogen is liberated instead, and potassium hydroxide remains in the liquid: $2K + 2HOH \rightarrow 2KOH + H_2$:

$$\text{Neg. Wire, } H_2 \text{ and KOH} \longleftarrow \text{K.Cl} \longrightarrow Cl_2\text{, Pos. Wire.}$$

We are confirmed in this explanation when we employ a solution containing a mixture of salts of copper and silver. The latter, being the less active metal, is first deposited, alone. The copper is liberated only after all the silver has been set free.

Having now before us the results of electrolyzing some typical substances, we bring these results into relation with the facts described in Chapter XVI. Acids contain hydrogen which possesses certain specific properties (p. 210), and by electrolysis all acids divide so as to give up *this constituent alone* at one electrode. The evidence that the other radical has different electrical properties which carry it to the opposite plate is conclusive. Again, salts undergo double decomposition in which they exchange radicals with acids, bases, and other salts (p. 211), and we find that it is **these very radicals which are withdrawn from the solution by the influence of the electricity.** Furthermore, the radicals exist free in the solution, being formed by dissociation of the molecules (p. 216). Hence **the function of the electricity seems simply to consist in sifting apart the two kinds of free radicals** which each solution contains. It only remains for us to explain in detail the sifting action of the current. Before turning to the explanation of this phenomenon, however, there is one question which may be answered in passing. Since a solution may eventually be cleared of all the hydrochloric acid, for example, which it contains, we should like to know how the free radicals in the center of the cell reach the electrodes.

Ionic Migration. — To know how the free radicals reach the electrodes, all that is necessary is to take a material, one (or both) of whose radicals is a colored substance, and watch the movement of the colored material as it drifts towards the electrode. Most salts which give colored solutions are suitable. In very dilute cupric sulphate solution, for example, a freezing-point determination shows that the depression has practically double the normal value. In other words, the dissociation into the radicals, $CuSO_4 \rightleftarrows (Cu) + (SO_4)$, is almost complete. Now, the blue color of the solution cannot be due to the few remaining molecules of $CuSO_4$, for anhydrous cupric sulphate is colorless. Nor is it due to the color of the (SO_4) radicals, for dilute potassium sulphate and dilute sulphuric acid are both colorless. On the other hand, all cupric salts, in dilute solution, have the same tint. The color is therefore that of the free cupric radical (Cu). In order most clearly to see the motion of the cupric radical, we place the cupric sulphate solution in the middle of the space between the electrodes, and place between it and the latter a colorless conducting solution. The motion of the blue material across the boundary may then be easily observed.

The most convenient arrangement is to dissolve the cupric sulphate in warm water containing about 5 per cent of agar-agar (a gelatine obtained in China from certain sea-weeds), and to fill with this mixture the lower part of a U-tube (Fig. 79). The setting of the jelly prevents subsequent mixing of the cupric sulphate system of materials with the rest of the filling of the tube, and the consequent disappearance of the boundary. A few grains of charcoal are scattered on the surface of the jelly to mark the present limits of the colored substance, and a solution of some colorless electrolyte, such as potassium nitrate, is added on each side. To prevent agitation of the liquid by the effervescence at the electrodes, it is well to use agar-agar with the lower part of the colorless liquid also. The whole is finally placed in ice and water, to prevent melting of the jelly by the heat caused by resistance, and the current is then turned on.

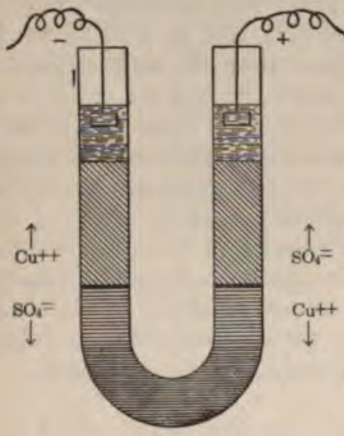

Fig. 79.

After a time, we observe that the blue cupric radicals ascend above the mark on the negative and descend away from it on the positive side. In each case there is no shading off in the tint. The motion of the whole aggregate of colored radicals occurs in such a way that, if the contents of the tube were not held in place by the jelly, we should believe that a gradual motion of the entire blue solution was being observed. With a current of 110 volts, and a 16-candle-power (one-half ampere) lamp in series with the cell, the effect becomes apparent in a few minutes.

Although the (SO_4) radicals are invisible, we may safely infer that they are drifting towards the positive electrode. Indeed, this can be demonstrated by interposing a shallow layer of jelly containing some barium salt a little distance above the charcoal layer on the positive side. When the (SO_4) reaches this, barium sulphate $BaSO_4$ begins to be precipitated and the layer becomes cloudy. In similar ways the progress of other colorless ions may be rendered visible.

It appears, therefore, that electrolysis is not a local phenomenon, going on round the electrodes only, but that the **whole of the products of the dissociation of the solute are set in motion.** It is on account of this remarkable property of traveling or **migrating** towards one or other of the electrodes that the individual atoms (like Cu), or groups of atoms (like SO_4), have been named **ions** (Gk., *going*). The term was first applied by Faraday to the materials liberated round the electrodes.

Different ionic substances move with different speeds when propelled by the same current. The hydrogen radical of acids (H) is the most speedy, the hydroxyl radical of bases (OH) comes next. These are, respectively, about five and two and one-half times as fast as any other ions. The actual speeds of several ions, in dilute solutions at 18°, when driven by a potential difference of 1 volt between plates 1 cm. apart, expressed in cm. per hour is: H 10.8, OH 5.6, Cu 1.6, SO_4 1.6, K 2.05, Cl 2.12.

The Nature of Ions: Faraday's Law. — That the molecules of certain classes of substances, although seemingly without chemical interaction with the water in which they are dissolved, should nevertheless be decomposed by the influence of the water, is strange, but not inconceivable. Heating produces a somewhat similar effect on many substances. The novel fact, for which an explanation is demanded, is that the molecules of the products of the dissociation appear to be attracted by electrically charged plates, which have been lowered into the solution, while molecules of dissolved sugar, for example, are not so attracted. Now the only bodies which we find to be conspicuously attracted by electrically charged objects are bodies which are *already provided with electric charges of their own.* Thus we are led to add the idea that substances which undergo dissociation in solution **divide themselves into** a special kind of **electrically charged molecules.**

Since the solution, as a whole, has itself no charge, **equal quantities of positive and negative electricity must be produced:**

$$HCl \rightleftarrows H^+ + Cl^- \quad NaCl \rightleftarrows Na^+ + Cl^- \quad NaOH \rightleftarrows Na^+ + OH^-.$$

This means that bivalent radicals, on dissociation, will become ions carrying a double charge and trivalent ions must carry a triple charge:

$$CuCl_2 \rightleftarrows Cu^{++} + 2Cl^- \qquad CuSO_4 \rightleftarrows Cu^{++} + SO_4^{=}$$
$$K_2SO_4 \rightleftarrows 2K^+ + SO_4^{=} \qquad FeCl_3 \rightleftarrows Fe^{+++} + 3Cl^-$$

In these equations, the coefficients multiply the charges as well as the radicals bearing the charges, and it will be seen that the numbers of + and − charges produced by each dissociation are equal. Hence, **univalent ions all possess equal quantities of electricity, and other ions bear quantities greater than this in proportion to their valence.** This is an inevitable inference from the electrical neutrality of all solutions. An **ion** is therefore **an atom or group of atoms bearing an electric charge.**

This conclusion is confirmed by actual measurement. When hydrochloric acid is electrolyzed, 35.46 g. (= Cl) of chlorine are liberated for every 1.008 g. (= H) of hydrogen. But when cupric chloride $CuCl_2$ is substituted, for every 35.46 g. (= Cl) of chlorine set free, only 31.78 g. ($= \frac{1}{2}$ Cu $= \frac{1}{2}$ 63.57) of copper is deposited. The **law,** discovered by **Faraday,** is that: **equal quantities of electricity liberate equivalent quantities of the ions** (equivalent, p. 65, not atomic or molecular).

To show that this view of the nature of the ions is adequate, we next apply it to the explanation of the phenomena of electrolysis. After that some seeming objections will be discussed.

Application to the Explanation of Electrolysis. — A battery is a machine which maintains two points, its poles, or two wires connected with them, at a constant difference of potential. One cell of a lead storage battery, for example, maintains a potential difference of about two volts. When the wires are joined, directly or indirectly, the poles are immediately discharged, but the cell continuously reproduces the difference in potential by generating fresh electricity. Now the effect of immersing two plates, one of which is kept by the battery at a definite positive potential and the other at a definite negative potential, into a liquid filled with multitudes of minute, suspended bodies, *already highly charged*, may easily be foreseen.

The figure (Fig. 80) will convey some idea of the behavior of the parts of a system such as we have imagined. The electrodes are marked − and +. The negatively charged plate attracts all the positively charged particles in the vessel and, although these particles were in continuous and irregular motion, they at once begin to drift toward the plate in question. On the other hand, the negatively charged particles are repelled by this plate and attracted by the positive plate, so that they drift in the opposite direction. Those which are nearest each plate, on coming in contact with it, will have their charges of electricity neutralized by the opposite charge on the plate, turning thereby into the ordinary free forms of the matter of which they are composed. The continuous removal of the electrical charges of the plates through contact with ions of the opposite charge furnishes occasion for recharging of the plate from the battery, and thus gives rise to a continuous current in each wire. Again, the continuous drifting of positively and negatively charged particles in opposite directions through the liquid, constitutes what, in the view of all external means of observation, appears to be an electical current in the liquid also. A magnetized needle, for example, which is deflected when brought near to one of the wires of the battery, is influenced in the same way by being brought over the liquid between the electrodes. The illusion, so to speak, of an electric *current* is complete, although in reality it is a *convection* of electricity that is taking place. Furthermore, the quantity of electricity being transported across any section of the whole system is the same as that

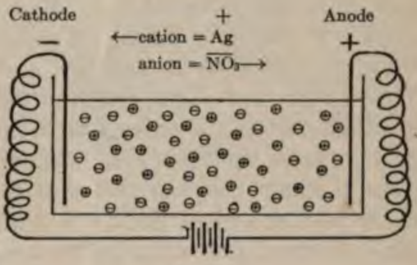

Fig. 80.

across any other, whether this section be taken through one of the wires, through the electrolyte, or even through the battery at any point. As fast as the ions are thus annihilated as such, the undissociated molecules (mingled with the ions, but not shown in the figure) dissociate and produce fresh ones, as in all chemical equilibria. Eventually, by continuing the process long enough, if the substances set free are actually deposited and do not go into solution again in any form, the liquid can be *entirely* deprived of the whole of the solute which it contains.

The analogy to the transportation of a fluid like water is noticeable, although not complete. Water may be transported in three ways. It may flow through a pipe, it may pass by pouring freely from one container to another, and it may be carried in vessels. Thus a stream of water, essentially continuous, might be arranged, in which part of the passage took place through the pipes, part by pouring from the pipes into buckets, and part by the carrying of those buckets between the ends of the pipes. The quantity of water passing a given point per minute in this system would be the same at every part, although the actual method by which the water was transported past the various points might be different. In such a disjointed circuit we suppose the electricity to move when carried from a battery through an electrolytic cell. It flows in the wire, passes by discharge between the pole and the ion, and is transported upon the ions in the liquid. The parallel is imperfect, however, because we have used the conception of *two* electric fluids and *because the ions are already charged in the solution, and before any connection with the battery is made.* They do not, so to speak, transport the electricity of the battery, but their own.

Questions Suggested by this Explanation. — 1. The question was raised (p. 217), as to how we can imagine separate atoms of sodium to exist in water without acting upon it, as the metal sodium usually does. But the ions of sodium in sodium chloride solution are *not* metallic sodium. They bear large charges of electricity. They possess an entirely different, and in fact, by measurement, much smaller amount of chemical energy than free sodium. And, as we have seen, the properties of a substance are determined as much by the energy it contains as by the kind of matter. Metallic sodium and ionic sodium are, simply, different substances. Besides, when metallic sodium acts on water, it turns into the ionic sodium of sodium hydroxide ($Na^+ + OH^- \rightleftarrows NaOH$). Ionic sodium ($Na^+$) from sodium chloride is, therefore, *already in* the very state which metallic sodium reaches by interaction with water, and is in no need of trying to enter that state.

2. We think of hydrogen chloride and common salt as exceedingly stable substances, and are averse to believing that precisely these compounds should be highly dissociated by mere solution in water. But it must be remembered that in solution they undergo chemical change very easily, and it is only in the dry form that they show unusual stability.

3. Again, why do not the ions combine, in response to the attractions of their charges? The answer is that they do combine, but the rate at which combination takes place is no greater than that at which the molecules decompose, so that on the whole the proportion of ions to molecules remains unchanged.

4. It might appear that the idea that bodies could retain high charges in the midst of water is contrary to all experience. It must be remembered, however, that the molecular, pure water, which separates the ions from one another, is a perfect nonconductor. The moisture which covers electrical apparatus and causes leakage of static electricity is not pure water, but a dilute solution, containing carbonic acid (p. 91) and materials from the glass of which the apparatus is made (p. 92). It conducts away the charge electrolytically, by means of the ions it contains, and not by itself acting as a conductor.

5. Finally, when we dissolve an electrically neutral salt in water, whence do the radicals obtain the electric charges? We now know that an atom, say, of sodium, contains a minute nucleus of positive electricity, which contains most of the mass of the atom. Outside of this nucleus, there are particles of negative electricity, called **electrons** (*q.v.*), each having a mass about one-eighteen hundredth ($\frac{1}{1800}$) of that of an atom of hydrogen. An ion of chlorine (Cl^-) consists, therefore, of an atom of chlorine *plus* one electron ($Cl + \epsilon$). An ion of sodium is an atom of sodium *minus* one electron ($Na - \epsilon$) and has thus an excess of one unit positive charge in the nucleus. When these two ions combine, the resulting molecule NaCl is neutral.

Résumé and Nomenclature. — The dissociation of molecules into ions is named **ionization.** The substances of the three classes which alone are ionized may be designated **ionogens.** An **ion** may be **defined** as, a molecule bearing negative or positive charges of electricity in proportion to its valence, and formed through the dissociation of an ionogen by a solvent like water.

Each molecule of the solute gives two kinds of ions with opposite charges. These two are forthwith distinct and independent substances, save that the attractions of the charges prevent any considerable separation by diffusion. They differ from non-ionic substances of the same material composition when such are known. The electrical charge is one of the essential constituents and, when it is removed, the properties alter entirely. Thus we have two kinds of hydrogen, gaseous molecular hydrogen (H_2), and ionic hydrogen (H^+), with entirely different chemical properties.

The radicals and their chemical behavior are real, and all the peculiarities of aqueous solutions of acids, bases, and salts are experimental facts. We now have experimental knowledge of the minute parts of bodies. Molecules are units which are not commonly disintegrated by vaporization (p. 102); ions, those which are not commonly disintegrated in double decomposition in solution; atoms, those which are not commonly disintegrated in any chemical action. The ionic explanation was first suggested as an hypothesis by Svante Arrhenius, a Swedish chemist, in 1887.

Since ionic hydrogen, ionic chlorine, etc., are entirely different in physical and chemical properties from the corresponding free elements, they should receive separate **names.** When it is inconvenient to say "ionic hydrogen," "ionic nitrate radical" (NO_3^-), etc., the following **names** will be used for the **ionic substances:**

Symbol.	Name of Substance	Anion of	Symbol.	Name of Substance.	Cation of Salts of
$SO_4^=$	Sulphate-ion	Sulphates	Na^+	Sodium-ion	Sodium
Cl^-	Chloride-ion	Chlorides	Fe^{+++}	Ferric-ion	Ferric iron
HSO_4^-	Hydrosulphate-ion	Bisulphates	NH_4^+	Ammonium-ion	Ammonium
OH^-	Hydroxide-ion	Hydroxides (bases)	Fe^{++}	Ferrous-ion	Ferrous iron
			H^+	Hydrogen-ion	Hydrogen (acids)

In using these terms, note that sodium-ion (with the hyphen) is the name of the *substance*, and not of the charged atom. When speaking in terms of ions as particles, therefore, we may not say "a sodium-ion," any more than we should say "an ionic sodium" or "ionic sodiums." To describe the charged molecule, we must write "a sodium ion," "sodium ions," "chlorate ions," etc.

Faraday distinguished the two kinds of material which proceed with and against the positive current by name. His terminology is still used. Ions which proceed in the same direction as the positive current (Fig. 80) are called **cations** (Gk., *down*). Such are H^+, Cu^{++}, K^+, NH_4^+. They are **metallic elements,** or groups which play the part of a metal. The electrode (Gk., *a path for electricity*) upon which they are deposited, the negative electrode, is spoken of as the **cathode** (Gk., *the way down*).

The particles which move in the direction of the negative current, and against that of the positive, are named **anions** (Gk., *up*). The ions Cl^-, NO_3^-, $SO_4^=$, MnO_4^- are of this kind. They are usually composed of **non-metals,** although sometimes, as in MnO_4^-, the constituents may be partially metallic. They are set free at the positive electrode, which is therefore named the **anode** (Gk., *the way up*). Chemists speak of metals and non-metals as **positive** and **negative elements,** respectively, even when electrical relations are not directly in question, and ions are not concerned.

Actual Quantities of Electricity Concerned. — The units of electrical energy are the **coulomb,** which is the unit of quantity, and the **volt,** which is the unit of difference of potential (or pressure, so to speak). Faraday's law has to do only with the former. Equal numbers of coulombs liberate equivalent weights of all elements, but different voltages are required to decompose different compounds, according to their stability (see Chap. XXXIX).

To liberate 1.008 g. of hydrogen, or one equivalent of any other element, 96,540 coulombs of electricity are needed. The charges on 1.008 g. of hydrogen ions must, therefore, equal this amount. There are 6.07×10^{23} molecules of hydrogen in 22.4 liters (H_2) and therefore in 2.016 g. of the gas. A simple calculation shows therefore that each coulomb is distributed over about 63×10^{17} ions of hydrogen.

A current of 1 coulomb per second is called 1 **ampere.** Thus, the current passing through a 1-amp. lamp (or 2 half-ampere 16-c.p. lamps in parallel) will liberate 1.008 g. (11.2 liters) of hydrogen in 96,540 seconds, or 26 hours and 49 minutes. The same current will liberate 107.88 g. of silver (Ag^{I}), or 31.78 g. of copper ($Cu^{II}/2$) from cupric sulphate in the same time. A current of 5 amperes will accomplish the same result in one-fifth of the time.

Applications: Ionic Equilibrium. — Since the ions are chemically different from their parent molecules, their formation represents a variety of chemical change. The change does not involve any chemical interaction with the water. It is simply a dissociation, *i.e.*, reversible decomposition of the dissolved substance.

From the fact that the proportion of molecules ionized is shown to become greater as more and more of the solvent is added (p. 215), and that removal of the solvent diminishes the proportion of ions to molecules, and finally leaves the substance entirely restored to the molecular condition, we know that this is a reversible action and therefore a true dissociation. The molecules and their ions adjust themselves like the constituents in any case of chemical equilibrium (pp. 177–182):

$$NaCl \rightleftarrows Na^+ + Cl^-.$$

The chemical behavior of substances in ionic equilibrium will be discussed in the next chapter (see p. 249).

* The mode of formulation previously used (p. 183) may be employed here. If [NaCl], [Na+], and [Cl−] stand for the molecular concentrations (numbers of moles per liter) at equilibrium of the molecules, and the two ions, respectively, we have an equilibrium constant (*cf.* p. 184), in this case called the **ionization constant:**

$$K = \frac{[Na^+] \times [Cl^-]}{[NaCl]}.$$

When we dissolve a single substance which gives only two ions, the molecular concentrations of the ions are necessarily equal. When some other ionogen with a common ion is present, however, the values of $[Na^+]$ and $[Cl^-]$ will be different.

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* The content of this paragraph is referred to in Chap. XX, but is not employed systematically until Chap. XXXV is reached.

Applications: To the Interpretation of Conductivity Measurements. — We have seen that when the solution of an ionogen is diluted, the proportion of ions to undissociated molecules increases, while removal of a part of the solvent has the opposite effect (p. 215). Now, a change in the number of ions naturally modifies the capacity of the liquid for carrying electricity, so that observation of the changes in the conductivity of a solution, when the concentration is altered, supplies the simplest means of studying the phenomena of ionization.

A glass trough and amperemeter * (Fig. 81) may be used to illustrate this principle. The electrodes are long strips of copper foil, which pass down at the ends of the trough. After placing the two instruments in circuit with a source of electricity, we first pour very pure water into the cell. With this arrangement, the amperemeter does not indicate the passage of any current of electricity. Concentrated (36 per cent) hydrochloric acid is next cautiously added through a long-stemmed dropping funnel, so that it forms a shallow layer below the water, and the funnel is withdrawn. The situation at this stage is that a definite amount of hydrogen chloride dissolved in a *small* amount of water fills what was before a nonconducting gap in the electric circuit. The deflection of the needle in the amperemeter indicates that a certain current of electricity is able to pass through this acid. When we now stir the

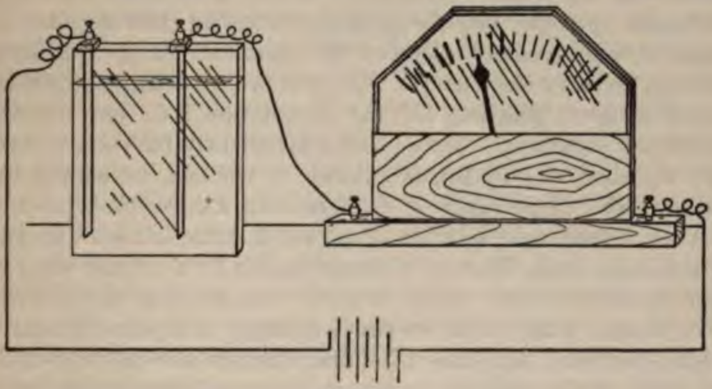

Fig. 81.

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* An amperemeter of low resistance, 0.5–1 ohm, must be used.

surface of the acid very gently with a thin glass rod, the amperemeter instantly responds, showing an increase in conductivity. As we stir, the conductivity increases, and the increase ceases only when the liquid has become homogeneous. Introduction of an additional supply of water will improve the conductivity still more, but the effect becomes less and less, until no change on further dilution is perceptible. Reasoning about these effects, we perceive that the *amount* of hydrochloric acid has not altered during the experiment. Yet the quantity of conducting material between the electrodes must have become greater, for the carrying power of the whole has improved. We were therefore observing the progress of a chemical change of the nonconducting hydrogen chloride into conducting materials. Hydrogen chloride molecules do not carry electricity (p. 145), but the hydrogen and the chloride ions, into which it was gradually altered by chemical change during the stirring, do carry electricity. Furthermore, the change practically ceased at great dilution, for the dissociation into ions was then practically complete. If we could conveniently have started with only liquefied, dry hydrogen chloride in the cell, we should have observed the whole range of changes from zero to the maximum.

When a saturated solution of cupric chloride is used instead of hydrochloric acid, dilution is accompanied by a similar improvement in conductivity. Here we notice, besides, that the yellowish-green liquid, with which we start, changes to a pale blue, as the yellowish-brown molecules of cupric chloride are dissociated and the color of the solution becomes more exclusively that of the copper ions. When the solution has become perfectly blue, further dilution is seen to affect the conductivity but slightly.

Reasoning still further about these phenomena we see that, if we start with a fixed amount of a given substance, the conductivities at different stages of the dilution *must be proportional to the numbers of ions*, and the maximum conductivity attainable by great dilution must represent the effect when *the whole material has become ionic*. Thus, if the conductivity at the maximum is represented, say, by 5, then at the dilution where the conductivity is 2, the proportion of the whole which is ionized is 2/5. When the conductivity becomes 4, 4/5 of the molecules are dissociated and the degree of ionization is 0.8. When the conductivity becomes 5, 5/5, or all, of the molecules are dissociated. For example, in hydrochloric acid, if we take the normal solution (p. 124) containing 36.5 g. of acid per liter as the unit of concentration, the fractions ionized at various concentrations are as follows: 10*N*, 0.17; *N*, 0.78; *N*/10, 0.91; *N*/100, 0.96. Thus, measurements of conductivity enable us to study the ionic decomposition of all ionogens, and to state accurately the fraction ionized, at each concentration, in solutions of every ionogen. This information is obviously most valuable, for it places us in a position to know the exact constitution of every solution we use in the laboratory. In the following section the data on which such knowledge can be based is given. In the next chapter the mode of applying the data is explained.

Constitution of Solutions of Ionogens: Fractions Ionized. — The **dilute acids** used in the laboratory are generally of six times normal (6*N*) concentration. But, often, we add only a drop or two to a large bulk of liquid, so that the acids are commonly very dilute as actually employed. The **solutions of salts** are of different strengths, but the great majority are of normal (*N*), or even smaller concentrations. In practice they, also, are still further considerably diluted before use. If, therefore, we give **the fractions ionized** (total molecules of ionogen = 1) **in decinormal solutions** (except where otherwise specified), the reader will be able to estimate roughly the proportion of each kind of ions in any application of the reagent. In the case of acids containing more than one displaceable hydrogen unit, the kind of ionization on which the figure is based is indicated by a period. Thus $H.HCO_3$ means that the whole of the ionization is assumed to be into H^+ and HCO_3^-.

FRACTION IONIZED IN 0.1*N* SOLUTIONS AT 18°

ACIDS

Nitric acid	0.92	Carbonic acid, $H.HCO_3$	0.0017
Nitric acid (conc., 62%)	0.09	Carbonic acid (*N*/25)	0.0021
Hydrochloric acid	0.92	Hydrogen sulphide, $H.HS$	0.0007
Hydrochloric acid (conc., 35%	0.13	Boric acid, $H.H_2BO_3$	0.0001
Sulphuric acid, $H.H.SO_4$	0.61	Hydrocyanic acid	0.0001
Sulphuric acid (conc., 95%)	0.01	Permanganic acid (*N*/2)	0.93
Hydrofluoric acid	0.15	Hydriodic acid (*N*/2)	0.90
Oxalic acid, $H.HC_2O_4$	0.50	Hydrobromic acid (*N*/2)	0.90
Tartaric acid, H.HT	0.08	Perchloric acid (*N*/2)	0.88
Acetic acid (*N*)	0.004	Chloric acid (*N*/2)	0.88
Acetic acid	0.013	Phosphoric acid, $H.H_2PO_4$	0.27
		Water	0.0_81

Bases

Potassium hydroxide	0.91	Ammonium hydroxide	0.013
Sodium hydroxide	0.91	Strontium hydroxide ($N/64$)	0.93
Barium hydroxide	0.77	Barium hydroxide ($N/64$)	0.92
Lithium hydroxide (N)	0.63	Calcium hydroxide ($N/64$)	0.90
Tetramethylammonium hydroxide ($N/16$)	0.96	Silver hydroxide ($N/1783$)	0.39
		Water	0.0_61

Salts

Potassium chloride	0.86	Sodium bicarbonate, $Na.HCO_3$	0.78
Potassium nitrate	0.83	Sodium phosphate, $Na_2.HPO_4$	0.73
Potassium acetate	0.83	Sodium tartrate	0.69
Potassium sulphate	0.72	Barium chloride	0.77
Potassium carbonate	(0.71)	Calcium sulphate ($N/100$)	0.64
Potassium chlorate	0.83	Cupric sulphate	0.39
Ammonium chloride	0.85	Silver nitrate	0.81
Sodium chloride (N)	0.66	Zinc sulphate	0.40
Sodium chloride ($N/2$)	0.74	Zinc chloride	0.73
Sodium chloride	0.84	Mercuric chloride	(<0.01)
Sodium nitrate	0.83	Mercuric cyanide	Minute
Sodium acetate	0.79		
Sodium sulphate	0.70		

In addition to their use in showing the nature of the reagents employed in the laboratory (p. 241), **these numbers show also to what extent any pair of ionic substances will unite when mixed** (see pp. 247, 251), and they likewise indicate the chemical activity of the ionogens when in solution (see next section).

Relation of Ionization to Chemical Activity. — These tables may be used for reference. The import of the following general statements, drawn from the tables, *should be memorized:*

1. **Salts,** with the exception of those of mercury, are all well ionized. In actions involving their ions, salts are therefore **all of the same order of activity,** for a dilute solution of every salt contains a large amount of the ionic components.

2. **Acids** show the most extreme differences in their degrees of ionization. That is to say their solutions must contain very different concentrations of hydrogen-ion. Since their activity as acids depends on this substance (p. 217), and the activity of a substance is proportional to its concentration (p. 182), it follows that **acids will show very great differences in apparent chemical activity.** At

this point, therefore, we emerge from semi-physical discussion of the subject and reach something of definite, practical application in chemical work.

The data show that acids may be divided roughly into **four classes** with different degrees of acidic activity:

(*a*) The ionization in decinormal solution exceeds 70 per cent; *e.g.*, nitric acid and hydrochloric acid. These are the acids which are chemically most active, for their solutions contain a relatively high concentration of hydrogen-ion.

(*b*) The ionization is between 70 and 10 per cent; *e.g.*, sulphuric acid and phosphoric acid. These acids are noticeably less active, for their solutions contain a lower concentration of hydrogen-ion.

(*c*) The ionization is between 10 and 1 per cent; *e.g.*, acetic acid. These are the weaker acids, for their solutions contain a very small concentration of hydrogen-ion.

(*d*) The ionization is less than 1 per cent; *e.g.*, carbonic and boric acids. These are the feeble acids, for their solutions contain only a minute concentration of hydrogen-ion.

3. The **bases** show **two classes:**

(*a*) Ionization high; *e.g.*, potassium hydroxide. These bases are active, for their solutions contain a high concentration of hydroxide-ion.

(*b*) Ionization less than 2 per cent; *e.g.*, ammonium hydroxide. These bases are weak on account of the low concentration of hydroxide-ion.

4. **Water** is less ionized than any other substance in the list. It shows therefore, as we already know, usually little or no interaction with acids, bases, or salts, and hence is valuable as a solvent for these substances. Its ions are H^+ and OH^-, and it is thus as much (or as little) an acid as a base.

Exercises. — 1. With solutions of the following substances, state, (*a*) what will be the products of electrolysis, (*b*) whether each is primary or secondary, and (*c*) how they may be isolated in each case: Potassium chlorate, potassium iodide, potassium iodate, silver sulphate, sodium peroxide.

2. Make equations (p. 232) showing the ionic and molecular materials in solutions of potassium bromide, potassium bromate, sodium periodate, aluminium chloride, zinc sulphate. Mark the

charges on the ions and give the name of each ionic substance (p. 236).

3. Prepare lists of other anions and cations which have been encountered, giving the formula and number of charges of electricity in each case.

4. If the conductivity of sodium chloride solution at the maximum is 110, and at greater concentrations is as follows: *N*, 74.7; *N*/10, 92.5; *N*/100, 103, calculate the fraction ionized at each concentration.

5. If the conductivity of acetic acid solution at the maximum is 352, and at greater concentrations is as follows: 10*N*, 0.05; *N*, 1.32; *N*/10, 4.6; *N*/100, 14.3, calculate the fraction ionized at each concentration.

6. If 1 c.c. of dilute hydrochloric acid (6*N*) is added to 30 c.c. of an aqueous solution, what is the reacting concentration of the acid?

7. Classify all the acids in the table (p. 241) according to the four classes (p. 243).

CHAPTER XIX

IONIC SUBSTANCES AND THEIR INTERACTIONS

In this chapter, after enumerating the various **classes of ionogens,** and the various **kinds of ionic substances,** we discuss the interactions of the latter. We consider first the relations of the ionic and the molecular substances (in equilibrium) when **a single ionogen** is present, and then take up the ways in which such **an ionic equilibrium is displaced.** Finally, we discuss some of the **useful** ionic interactions, in which the equilibria are displaced so far that practically complete interaction occurs: namely, **precipitation, neutralization,** and **displacement.**

The Classes of Ionogens. — **Acids** are classified according to the number of hydrogen units in their molecules. Thus chloric acid $HClO_3$ is a **monobasic acid,** sulphuric acid H_2SO_4 a **dibasic acid,** and phosphoric acid H_3PO_4 a **tribasic acid.** These terms relate to the fact that, in neutralization (see p. 254) the acids interact with one, two, or three molecules of a base like sodium hydroxide.

Bases are named in a similar way: sodium hydroxide $NaOH$ is a **monoacid base,** calcium hydroxide $Ca(OH)_2$ is a **diacid base.**

Salts like KCl and Na_2CO_3 are **neutral** (see acid salts, below) or **normal salts,** and $NaKCO_3$ and $Ca(OCl)Cl$ (bleaching powder) are **mixed salts.**

The most interesting classes of mixed salts are the **acid salts** (p. 206) and the **basic salts.** In acid salts, like $NaHSO_4$ (p. 141) and KH_2PO_4 (p. 196), all the hydrogen of the acid has not been replaced by a metal. In basic salts, like $Ca(OH)Cl$, part of the basic hydroxyl remains.

There are also many **double salts,** like ferrous-ammonium sulphate $(NH_4)_2SO_4,FeSO_4,6H_2O$, and alum (see index), some of which are in common use.

All these substances are ionogens (p. 236). The mixed and double salts are, naturally, dissociated into more than two ionic substances.

Ionic Substances Furnished by Acids. — The mode of naming ionic substances has already been given (p. 236).

Acids, *e.g.*, HCl, H_2SO_4, when dissolved in water, all furnish hydrogen-ion H^+ and a negative ionic substance (anion), *e.g.*, Cl^-, $SO_4^=$. The solutions differ from those of salts in the constant presence of hydrogen-ion, and in the absence of any other positive ion.

Hydrogen-ion H^+ is a colorless substance. It is sour in taste, and its presence is recognized by the fact that it turns blue litmus red (see Indicators, below). These properties serve as **tests** for acids, as they are not interfered with by other ionic substances which may be present. Hydrogen-ion is univalent and, when combined with negative radicals of salts, gives the (molecular) acids. The activity of acids depends upon the concentration of the hydrogen-ion they furnish (p. 242), and therefore upon their solubility and the degree of ionization of the dissolved molecules. Some furnish so little hydrogen-ion that their action on litmus can hardly be detected.

Ionic Substances Furnished by Bases. — **Bases,** *e.g.*, KOH, NH_4OH, $Zn(OH)_2$, all furnish hydroxide-ion OH^- and some positive ionic substance (cation), K^+, NH_4^+, Zn^{++}. Their solutions differ from those of salts in the constant presence of hydroxide-ion and in the absence of any other anion. The more active bases, that is, those which are soluble and highly dissociated, so that they give a high concentration of hydroxide-ion, are called **alkalies.** Such are potassium and sodium hydroxides. They are often named caustic alkalies and, individually, caustic potash and caustic soda. The solutions are called lyes.

Hydroxide-ion OH^- is a colorless substance. Properties which serve as **tests** for bases are that hydroxide-ion possesses a soapy taste and feeling and turns red litmus blue (see Indicators, below). It is univalent, and combines with positive radicals to form (molecular) bases.

Ionic Substances Furnished by Salts. — **Salts** furnish positive and negative ionic substances, which may be either simple or composite, $Na.Cl$, $Na.NO_3$, $NH_4.Cl$, $NH_4.NO_3$. Some ionic substances are colored, Cu^{++} (cupric-ion) blue, Cr^{+++} reddish-violet, Co^{++} pink, MnO_4^- (permanganate-ion) purple, $Cr_2O_7^=$ (dichromate-ion) orange, but most of them are colorless, K^+, Na^+, Zn^{++}, Cl^-, I^-, NO_3^-, $SO_4^=$. They vary in taste, some being salt, some astringent, some bitter. The ionic materials characteristic of salts do not affect litmus, and individual **tests** are required for each. Usually we add some other ionic substance, with which the ion thought to be present combines to form an insoluble, molecular substance of known color, or appearance, and examine the precipitate if any appears. Thus, when the presence of chloride-ion Cl^- is suspected, we may add a solution containing silver-ion Ag^+, expecting to obtain a precipitate of silver chloride AgCl ($Cl^- + Ag^+ \rightarrow AgCl\downarrow$). In dilute solutions of *salts*, the ions are almost *always* numerous in comparison with the molecules (p. 242), so that salts are practically all active and their solutions almost always respond readily to the tests for the ions they contain. The art of detecting the various ionic substances present in a solution constitutes a large part of the branch of chemistry called qualitative analysis.

All the known ionic substances are found in solutions of salts. The only ions which are not characteristic of salts, although sometimes occurring in their solutions (see acid and basic salts, above), are hydrogen-ion H^+, and hydroxide-ion OH^-.

It will assist the reader if the following facts are kept in mind. The elements which can form a simple positive ion are the **metallic** elements (p. 94, and see Chaps. XXII and XXXIII). **Non-metallic** elements, like nitrogen, may be present in a positive ion, as in NH_4^+, but never exclusively. In other words, we know no such substances as nitrogen sulphate, or carbon nitrate. Conversely, the metals are frequently found in the negative ion, but never constitute it exclusively. They are then usually associated with oxygen, as in MnO_4^-, and $Cr_2O_7^=$.

The Ionic Equilibrium with a Single Ionogen. — In the ionization of a molecular substance, the chemical change is incomplete and the system reaches a condition of equilibrium (p. 238). The action is, therefore, reversible, and there are thus **two routes** to the same equilibrium point. This fact must not be forgotten, for we have to consider the union of ionic substances even more often than the converse change. Now, the **degrees of ionization** of various ionogens **tell us** the location of the equilibrium point, and therefore

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the extent of the chemical change involved in reaching this point by *either route*, that is, either by the dissociation of molecules or by the union of ions. In a class of interactions, of which all are incomplete, and only those are interesting and useful which approach completeness, we require some means of knowing which are complete and why they are so. The table of fractions ionized (p. 241) supplies most of the required information.

To illustrate, take the case of a single ionogen. When we place hydrogen chloride in decinormal solution, 0.92 of the molecules dissociate. Conversely, when we start with the hydrogen-ion and chloride-ion, say by mixing two solutions, each of which contains one of them (along with another ion), then 1 − 0.92, or only 0.08 of these ionic substances will combine.

This exemplifies the case of an active acid. The following equations show the data for six typical substances in $N/10$ solution, namely, two acids, two bases, and two salts:

$$
\begin{array}{ll}
(8\%)HCl \rightleftarrows H^+ + Cl^-(92\%), & (98.7\%)HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-(1.3\%) \\
(9\%)KOH \rightleftarrows K^+ + OH^-(91\%), & (98.7\%)NH_4OH \rightleftarrows NH_4^+ + OH^-(1.3\%) \\
(16\%)NaCl \rightleftarrows Na^+ + Cl^-(84\%), & (61\%)CuSO_4 \rightleftarrows Cu^{++} + SO_4^=(39\%)
\end{array}
$$

These samples are chosen to illustrate, in each pair, the extremes. Thus, when potassium-ion and hydroxide-ion are brought together little union takes place, while with ammonium-ion and hydroxide-ion the union is practically complete. In the case of the soluble *salts*, however, there are almost (p. 242) no cases of considerable union of the ions in dilute solutions. The case of water, on the other hand, is one of the most extreme:

$$(99.9_5\%)\ H_2O \rightleftarrows H^+ + OH^-\ (0.0_41\%).$$

Hydroxide-ion and hydrogen-ion thus unite almost completely.

Similar reasoning enables us to handle the more complex, but very common case of the mixing of two ionogens. The degrees of ionization tell us the exact condition of each system separately, before mixing. The result of the mixing is best understood by viewing the change as consisting in a *displacement* of each of the equilibria by the action of the components of the other. We consider, therefore, next, the displacement of ionic equilibria.

The Displacement of Ionic Equilibria. — Equilibria are displaced by changes which favor or disfavor one of the opposed actions (p. 180). There may be either, (1) a physical change in the conditions, or a chemical interaction which (2) adds to, or (3) removes one of the interacting substances. Each of these may be illustrated in turn.

1. As an example of the first, we have the **effect of changing the amount of the solvent** (p. 215). Adding more of the solvent reduces the concentration of the ionic materials and disfavors their union, so that it indirectly promotes dissociation. The larger the volume in which the ions are scattered, the less often will they meet, and the smaller the amount of combination. On the other hand, evaporating off a part of the solvent favors the encounters of the ions and promotes combination. When the solvent is at last entirely gone, the whole material is molecular.

In cases where the ionic and molecular substances are all colorless, these changes can be followed only by a study of the freezing-points or other similar properties of the solutions (p. 216). But when the substances are of different colors, the changes can also be seen. Thus, cupric bromide in the solid form is a jet black, shining, crystalline substance. When treated with a small amount of water it forms a solution which is of a deep reddish-brown tint, giving no hint of resemblance to a solution of any cupric salt. This doubtless represents the color of the molecules. When more water is added, the deep brown gives place gradually to green, and finally to blue. The latter is the color of the cupric-ion (Cu^{++}), and is familiar in all solutions of cupric salts. The colorless nature of solutions of potassium and sodium bromides shows that bromide-ion (Br^-) is without color. Hence, in the present instance it is invisible. We are thus watching the forward displacement of the equilibrium:

$$CuBr_2 \text{ (brown)} \leftrightarrows Cu^{++} \text{ (blue)} + 2Br^-.$$

If 1 g. of the solid is taken, it dissolves in about its own weight of water, and independent measurement shows that there is relatively little ionization. Hence the solution is deep brown. When 10 c.c. of water has been added, 70 per cent of the salt is ionized, and the solution is green. With 40 c.c. of water, only 19 per cent remains in molecular form, and the blue color of the cupric-ion entirely overbears the tint of the molecules. If we now remove the water by evaporation, all these changes are reversed. When 30 c.c. of the water has been driven off, the solution is green. As the evaporation of the remaining 10 c.c. progresses, the brown color appears. When the water is all gone, the black residue remains. Here we are observing the backward displacement of the equilibrium, $CuBr_2 \leftrightarrows Cu^{++} + 2Br^-$.

2. Cupric bromide may be used to illustrate also the chemical methods of displacing equilibria. Thus, we may show the **effect of adding more of one of the reacting substances.** If, at the green stage, we dissolve solid potassium bromide in the liquid ($KBr \rightleftarrows K^+ + Br^-$), the increased concentration of bromide-ion causes more vigorous interaction of the ions, and the molecules, with their brown color, become prominent again. Adding cupric chloride increases the concentration of cupric-ion and has the same effect. In either case, renewed dilution with water reduces the concentrations of all the ions once more, the molecules become fewer, and the brown color is displaced by the blue for the second time.

3. Finally, the displacement of the same equilibrium **by removing one of the interacting substances** may be illustrated. Thus, if the chocolate-brown solution, in which molecular cupric bromide predominates, is shaken with pulverized lead nitrate (and filtered), two changes are noticed. A pale yellow precipitate of lead bromide appears ($Pb^{++} + 2Br^- \rightarrow PbBr_2 \downarrow$), and the *brown color fades into green*. Here the displacement is the opposite of the last. Instead of reinforcing one of the ions, we have reduced the concentration, and in fact almost entirely removed one of them, namely Br^-. This has, naturally, stopped the interaction of the Cu^{++} and Br^- which reproduces the brown, molecular $CuBr_2$. Hence the dissociation of the latter has continued to exhaustion of the whole molecular material.

The reader will find that the behavior of these ionic equilibria, and the way in which we discuss and explain it, are complete parallels of the behavior and explanation in the case of ordinary equilibria (pp. 185–187), which should now be reëxamined. The illustrations in the present section, and particularly the third (*cf.* p. 203), should be considered until every feature is perfectly clear. They furnish the key to understanding the applications which follow. One fact must not escape notice, and that is that in none of the three instances was the forward action (the dissociation) in itself affected. The molecules of cupric bromide have, as we should expect, a certain tendency to decompose. No encounters between these molecules are required for mere decomposition. Hence their decomposition is not influenced by their nearness to, or remoteness from, one another (illustration 1), nor by the presence of any other kinds of molecules or ions (illustrations 2 and 3). The effect, whether it involved an apparent increase, or a diminution of the dissociation, *was always accomplished by altering the concentration of the ionic substances, and therefore the activity of the reverse action.*

Applications: Double Decomposition in Solution. — We are now prepared to consider the general case of mixing the solutions of *two* ionogens.

When solutions of two ionized substances are mixed, the first reflection which occurs to us is that each of these has been diluted by the water in which the other was dissolved, so that the first effect will be to increase the degree of ionization of both to a certain extent.

The next consideration is, however, that we have produced a mixture of four ions, which must have at least some tendency to unite crosswise. Thus potassium chloride and sodium nitrate in dilute solution are very greatly ionized before mixing. The reversible actions, represented by the horizontal pair of the following equations, have taken place extensively. But, by mixing the liquids, we have brought into presence of one another two new pairs of positive and negative ions. Hence, two other reversible actions, the vertical ones, will be set up and will proceed until a fresh equilibrium of all the ions with all four kinds of molecules has been reached. Thus far the description will fit any case of mixing solutions of two ionogens.

$$\begin{array}{rcccc} KCl & \leftrightarrows & K^+ & + & Cl^- \\ NaNO_3 & \leftrightarrows & NO_3^- & + & Na^+ \\ & & \downarrow\uparrow & & \downarrow\uparrow \\ & & KNO_3 & & NaCl \end{array}$$

Now, in this particular instance, what is the actual extent of such interaction as has occurred? To answer this question we require to know the proportion of molecules to ions in a solution of each of the four salts (p. 242). In decinormal solutions it is KCl, 14 : 86; $NaNO_3$, 17 : 83; KNO_3, 17 : 83, NaCl, 16 : 84, so that the salts are all equally well ionized. It is a good plan to add these proportions in the formulation. Furthermore, in a *dilute* mixture, such as we are considering, the *proportions of ions are greater than* *these figures indicate.* Hence, practically no chemical action has occurred.

$$\begin{array}{rcccl}
 & & (>83\%) & & (>84\%) \\
(14\%)\mathrm{KCl} & \rightleftarrows & \mathrm{K^+} & + & \mathrm{Cl^-}\ (86\%) \\
(17\%)\mathrm{NaNO_3} & \rightleftarrows & \mathrm{NO_3^-} & + & \mathrm{Na^+}\ (83\%) \\
 & & \downarrow\uparrow & & \downarrow\uparrow \\
 & & \mathrm{KNO_3} & & \mathrm{NaCl} \\
 & & (<17\%) & & (<16\%)
\end{array}$$

That this inference is correct is shown by independent evidence. Thus when the solutions of salts are mixed, **no thermal effect** is observable. This fact has been known since 1842 as Hess' **law of thermoneutrality.** Again, if the solutions are placed in a cell (Fig. 81, p. 239), so that the one forms a layer below the other, no change in conductivity is noticed when the solutions are stirred together. Hence no change in the number of ions has occurred.

We conclude, then, that when two highly ionized substances are mixed, **and the possible products are also highly ionized, soluble substances,** then **practically no chemical action occurs.** This rule applies to dilute solutions of all soluble salts (p. 242) and to mixing salts with the highly ionized acids or bases.

Conversely, when two ionized substances are mixed, **an extensive chemical change does ensue in two cases,** namely:

1. When one of the possible products is an insoluble substance and **precipitation** occurs, for this removes the ions used to form the insoluble body.

2. When one of the possible products, although soluble, is **little ionized,** as in **neutralization,** for this likewise removes the ions required to form molecules of the product. We proceed, therefore, to discuss these two important classes of actions.

Precipitation. — A typical case of precipitation occurs when we mix dilute solutions of silver nitrate and sodium chloride.

$$\begin{array}{rcccl}
 & & (>83\%) & & \\
(16\%)\ \mathrm{NaCl} & \rightleftarrows & \mathrm{Na^+} & + & \mathrm{Cl^-}\ (84\%) \\
(19\%)\ \mathrm{AgNO_3} & \rightleftarrows & \mathrm{NO^-_3} & + & \mathrm{Ag^+}\ (81\%) \\
 & & \downarrow\uparrow & & \downarrow\uparrow \\
 & & \mathrm{NaNO_3} & & \mathrm{AgCl}\ (\text{dslvd}) \\
 & & (<17\%) & & \downarrow\uparrow \\
 & & & & \mathrm{AgCl}\ (\text{solid})
\end{array}$$

Here, since the four substances are all *salts*, they are all highly ionized. If they were all soluble, then, in dilute solutions, perhaps 5 per cent of each salt would be in molecules and the rest in ionic form. But the *molecules of silver chloride are excessively insoluble.* **In all cases of precipitation, we look up the solubilities of the possible products** (see Table of Solubilities inside the front cover). Here we find that one liter of water will dissolve only 0.0016 g. silver chloride (this quantity includes *both* ions and molecules). So the concentration of the AgCl (dslvd) becomes almost zero through precipitation. **So far as it is in solution,** however, being a salt and very dilute, **it is practically all ionized.** The precipitation displaces the equilibrium, for, the dissociation having thus ceased, those of the ions Ag^+ and Cl^- which combine are not replaced by others. Hence the silver-ion and chloride-ion almost disappear. This occurrence affects in turn the equilibria with Na^+ and NO_3^-, so that the NaCl and $AgNO_3$ become completely ionized. Hence the concentrations of NaCl and $AgNO_3$, of Ag^+ and Cl^-, and of the dissolved AgCl, all become practically zero at last. The system finally contains only a precipitate of molecular, solid silver chloride and a solution of the three substances, $Na^+ + NO_3^- \leftrightarrows NaNO_3$, in equilibrium. By far the greater part of this material in solution is the ionic, namely the Na^+ and the NO_3^-.

To avoid a misconception, note that the answer to the question, "Is silver chloride a highly ionized substance?" is "Yes." Since it is a salt, we expect this. True, very little of it dissolves, so that it cannot give many ions to a solution. But little or much ionized refers to the proportion ionized of the material which *has* dissolved. With undissolved material ionization has nothing to do.

It should be noted that, when the solutions are mixed, as in the foregoing example, strictly speaking, the chief *interaction* taking place is the production of the *insoluble body*. The largest part of the chemical action may be formulated thus:

$$Ag^+ + Cl^- \rightarrow AgCl.$$

The chief change that has as yet befallen the ions of sodium nitrate is that they have been transferred from two separate vessels into one. Potentially the salt has been formed. But the actual union of its ions, to give the second product in the molecular condition,

$$Na^+ + NO_3^- \rightarrow NaNO_3,$$

comes about only when, at some subsequent time, if at all, the water is evaporated away.

The foregoing formulation and explanation apply to every case of mixing ionogens where precipitation occurs, that is, where the products are insoluble acids, bases, or salts.

Neutralization. — We may now consider the case of **mixing solutions of two ionogens** where one is **an acid** and one **a base.**

$$\begin{array}{rcccl} & & (>87\%) & (.0_41\%) & \\ (8\%)\ \mathrm{HCl} & \leftrightarrows & \mathrm{Cl}^- & +\ \mathrm{H}^+ & (92\%) \\ (9\%)\ \mathrm{NaOH} & \leftrightarrows & \mathrm{Na}^+ & +\ \mathrm{OH}^- & (91\%) \\ & & \downarrow\uparrow & \downarrow\uparrow & \\ & & \mathrm{NaCl} & \mathrm{H_2O} & \\ & & (<13\%) & (100\%) & \end{array}$$

The general plan of all interactions of acids and bases is shown in the formulation. The ionization of the hydrochloric acid reaches 0.92 in a decinormal solution, and goes farther when the acid is diluted with the water of another solution. That of the sodium hydroxide similarly goes beyond 0.91. Thus the substances in the solutions before mixing are almost entirely ionic. The crosswise union, $H^+ + OH^- \leftrightarrows H_2O$, however, is all but complete, for water is hardly ionized at all (p. 243). The materials on whose interaction with the Cl^- and Na^+, respectively, the maintenance of the molecules HCl and NaOH depends, being thus removed, the dissociation of the acid and base promptly brings itself to completion, and the left sides of the equations vanish. Practically all the hydrogen-ion and hydroxide-ion become water, which thenceforth is simply a part of the solvent. The Cl^- and Na^+, however, if the solution is now 1/20 normal, unite to the extent of 0.13 only. If it is more dilute, this union forms a still smaller factor in the whole change. Practically it is negligible. Now all that has been said of *this* acid and base will apply *mutatis mutandis* whenever any active, highly ionized acid and base come together. Thus we may write **one simple equation for all neutralizations of active acids and bases:**

$$H^+ + OH^- \rightarrow H_2O,$$

without omitting anything essential.

The ions of a salt are always left over from the main action, and may be brought together, in turn, by evaporation: $Na^+ + Cl^- \rightarrow NaCl$, or the liquid may be used as a solution of the pure salt.

Confirmations of this View of Neutralization. — That these inferences are correct is shown by many facts. The most conspicuous of these is the fact that, when *equivalent* amounts of *active* acids and bases are used, the mixture is *without action* either *on red or on blue litmus.* It is **neutral** to indicators — hence the term **neutralization** applied to the operation of mixing an acid and a base. Specifically, the absence of effect upon litmus demonstrates the absence of hydrogen-ion H^+ and of hydroxide-ion OH^-, alike, in the product, and confirms the theory.

Again, a considerable thermal effect accompanies neutralization. But, in the cases we are discussing, that is where *active* bases and acids are employed, the heat liberated by use of equivalent weights (p. 124) is *always the same,* namely 13,700 cal. That it is always the same confirms our theory, for practically the whole change is always the formation of 18 g. of water from the ions.

Still again, when we place the acid and base in the cell (Fig. 81, p. 239), so that the one forms a layer beneath the other, and watch the amperemeter while we mix the solutions, a marked *decrease* in the current passing through the cell is noticed. This also confirms our theory, for it is our belief that one-half of the ions, namely the H^+ and OH^-, disappear as such during the action. The decrease is, in fact, to less than half the reading before mixing, because the two speediest ions have been removed.

When less highly ionized acids or bases are used, the only difference is that there are more of the molecular materials present, before the solutions are mixed. But the removal of the H^+ and OH^- ions permits the molecules of the acid and base to dissociate, so that the final products are water and the ions of a salt, as before.

The foregoing formulation and explanation apply to every case of mixing ionogens, where a very slightly ionized substance is one of the products, that is, when water, or a feeble acid, or a feeble base (pp. 242–243) is formed.

Acidimetry and Alkalimetry. — When, as is constantly the case, a chemist desires to ascertain the **quantity** of an acid or base present in a solution, he uses for the purpose the interaction just discussed. If, for example, the problem is to ascertain the weight of hydrogen chloride in each liter of a specimen of hydrochloric acid, this can be done by neutralizing a measured portion of this acid with a solution of an alkali of *known concentration*. The volume of the latter which is required for the purpose is observed. If the alkali is sodium hydroxide, the action taking place is

$$HCl + NaOH \rightarrow H_2O + NaCl.$$

The volume of acid is measured out into a beaker by means of a pipette (Fig. 82) of fixed capacity, which is filled by suction to the mark on the stem. Suppose the amount to be 25 cc. The standard alkali solution is placed in a burette (Fig. 83), which is filled down to the tip of the nozzle. A few drops of litmus solution are now added to the acid, and the alkali is allowed to run in slowly. After a time, the hydroxide-ion which this introduces will begin to produce a blue color, close to where the stream enters the liquid. This is at first dissipated by stirring, and the whole remains red. Finally, however, a point is reached at which the entire solution assumes a tint intermediate between blue and red. With one drop less of the base, it is distinctly red. With one drop more, it would become distinctly blue. Litmus paper of either shade dipped in this neutral solution remains unaffected.

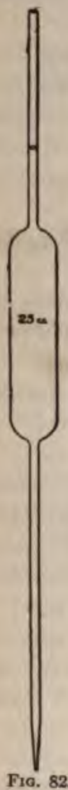

FIG. 82.

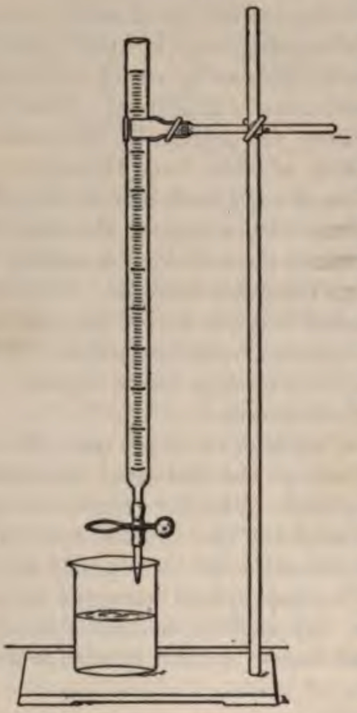

FIG. 83.

By the use of a standard solution of an acid in the burette, the quantity of a base may be determined in the same way.

Standard Solutions. — The **standard solutions** used in this work are usually normal, and contain one equivalent weight of the alkali or acid in one liter of the solution. For more delicate work, decinormal (N/10) solutions may be employed. The concentration of such a solution is called its **titer,** and the operation of analyzing another solution by means of it, **titration.** The value of standard solutions lies in the fact that, when once the solution has been prepared, and the exact concentration adjusted by quantitative experiments, its use does not require any weighing, and the measurements of volumes can be carried out with great rapidity.

The **calculation of the result** is also simple. One liter of normal alkali contains 17 g. of available hydroxyl, and one liter of normal acid, 1 g. of available hydrogen (p. 124). Equal volumes of normal solutions will therefore exactly neutralize one another, 18 g. of water being formed by interaction of a liter of each. If, for the neutralization of the 25 c.c. of hydrochloric acid used above, 50 c.c. of normal alkali are required, the acid is twice-normal ($2N$). When 15 c.c. are required, the acid is $\frac{15}{25}$ or $\frac{3}{5}N$. If the actual weight of the acid in the latter case has to be calculated, we remember that there are 36.46 g. of hydrogen chloride in 1 l. of a normal solution, and therefore $36.46 \times \frac{3}{5} \times \frac{25}{1000}$ g. = 0.5467 g. in 25 c.c. of a solution which is $\frac{3}{5}$-normal.

Methods of quantitative analysis in which standard solutions are employed are known as **volumetric** methods, and are much used by analysts and investigators. They occupy much less time than **gravimetric** operations, in which numerous weighings have to be made, and are often just as accurate. The substances, like litmus, by whose change of color the completeness of the action is made known, are called *indicators.*

Indicators. — Indicators are substances which, in presence of certain other substances, assume a very deep color, or change sharply from one deep color to another. Thus, phenolphthaleïn is colorless in presence of acids (*i.e.*, hydrogen-ion), and red (when dilute, pink) in presence of alkalies (*i.e.*, hydroxide-ion). Litmus, again, is red with acids, and blue with alkalies. The change of color depends upon a chemical interaction in each case, but since indicators are chosen for their strong coloration, the quantity of the acids or base used up in changing the tint of the trace of the indicator is so small as to be negligible. The common indicators are:

Phenolphthaleïn $C_{20}H_{14}O_4$, a colorless substance and very feeble acid. It is not perceptibly dissociated into its ions,

$$C_{20}H_{14}O_4 \text{ (colorless)} \leftrightarrows C_{20}H_{13}O_4^- \text{ (red)} + H^+,$$

and in neutral or acid solutions is, therefore, without visible color. When a base is added gradually to an acid containing some of this indicator, the acid is first neutralized. Then, and not till then, the slightest excess of hydroxide-ion unites with the trace of hydrogen-ion from the phenolphthaleïn, the above equilibrium is displaced forwards, and a visible amount of the red negative ion is formed:

$$\left.\begin{array}{llll} C_{20}H_{14}O_4 \text{ (colorless)} & \leftrightarrows C_{20}H_{13}O_4^- & \text{(red)} & + H^+ \\ NaOH & \leftrightarrows Na^+ & & + OH^- \end{array}\right\} \leftrightarrows H_2O.$$

In this more compact formulation, we show the product (H_2O) from the union of the two ions which combine, but omit the product from the union of Na^+ and $C_{20}H_{13}O_4^-$, because here (since the product is a salt) hardly any union occurs.

Litmus is an extract from certain lichens, first used by Boyle. It contains azolitmin. One of its colors is that of the molecule, and the other that of the ion.

Methyl orange $(CH_3)_2NC_6H_4.N : N.C_6H_4SO_3Na$ is a complex organic compound which gives, in acid solution, a red, and in alkaline solution a yellow color.

Congo red is the sodium salt of an acid of complex structure (see Dyes). In neutral or alkaline solutions it is red; with acids it turns blue. Paper dipped in Congo red differs from litmus paper in that it shows gradations in color, the blue being much more distinct with an active acid than with a relatively weak one like acetic acid (p. 241). Litmus paper is equally red with all acids save the very feeblest.

Displacement: The Electromotive Series. — In the preceding sections we have dealt with cases in which ionic substances **underwent combination or ionogens dissociated.** This is one of **five kinds of ionic chemical change.** Of the remaining four, **ionic dis-**

placement is the one * that we have most frequently encountered. Thus, certain metals displace hydrogen from dilute acids (p. 60):

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2.$$

These interactions do not occur in the absence of water (p. 53), and now appear in a new light, namely, as ionic actions:

$$Zn + 2H^+ + SO_4^= \rightarrow Zn^{++} + H_2 + SO_4^=.$$

The molecular sulphuric acid and zinc sulphate, which are small in amount, are omitted because they do not, as such, take part in the change. On looking at the equation, we perceive that the sulphate-ion is also unaltered by the action, and may be left out likewise:

$$Zn + 2H^+ \rightarrow Zn^{++} + H_2.$$

True, hydrogen-ion cannot be used alone, for it is always accompanied by *some* negative radical. But the latter, like the vessel in which the experiment is made, is part of the necessary apparatus, and not an interacting substance. The change has consisted in the ionization of the zinc, and the transfer to it of the electric charge of the hydrogen-ion. In terms of electrons (p. 235), each atom of zinc has lost two electrons ($Zn - 2\epsilon = Zn^{++}$) and two ions of hydrogen have taken up the electrons ($2H^+ + 2\epsilon \rightarrow H_2$).

These statements enable us to understand why active acids, with zinc, give hydrogen faster than do inactive acids (p. 54). The former provide a higher concentration (p. 243) of hydrogen-ion, that is, of the real interacting substance, than do the latter.

A similar displacement of negative ions has been met with (pp. 194, 199). Thus, chlorine displaces bromine from solutions containing bromide-ion.

$$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2.$$

The Electromotive Series. — Displacement occurs with all positive ions. Thus, zinc will displace other metallic elements, such as iron, lead, copper, and silver, from the ionic conditions, when it is placed in solutions of their salts:

$$Zn + Cu^{++} \rightarrow Zn^{++} + Cu.$$

---

* The **discharge of an ion** and liberation of its material in **electrolysis** (pp. 55, 155, 227) is another. Attention will be called to the remaining two when suitable illustrations occur (see pp. 270, 504).

Here the copper appears as a red precipitate. Lead, in turn, will displace copper and silver, but not zinc or iron. Copper will displace silver. Thus the metals can be set down in an order, such that each metal displaces those following it in the list and is displaced by those preceding it. This list is known as the **electromotive series** of the metals, because in electrolysis of normal solutions of their salts, the electromotive force of the current required to deposit each metal is less than that for the metal preceding in the list. For present purposes, the list shows the metals in **the order of diminishing tendency to enter the ionic from the elementary condition.**

Electromotive Series of the Metals.

Potassium
Sodium
Barium
Strontium
Calcium
Magnesium
Aluminium
Manganese
Zinc
Chromium
Cadmium
Iron
Cobalt
Nickel
Tin
Lead
Hydrogen
Copper
Arsenic
Bismuth
Antimony
Mercury
Silver
Palladium
Platinum
Gold

The electromotive series embodies many facts in the behavior of the metals, and should be kept in mind as **furnishing a key to all actions involving solutions in which a *free metal* is used or produced.** It is, in fact, identical with the order of activity (p. 60).

To avoid a common misconception, it must be noted that the electromotive series cannot be used to explain the tendency of one radical to dislodge another in double decompositions. The place of an element in the E.M. series defines its relative activity *when free*, and has to do only with actions where *one free element displaces* (p. 55) *another*. The influences which determine a double decomposition (*cf*. pp. 143, 186) are such as the insolubility of a compound. Thus, potassium bromide solution will slowly convert a precipitate of silver chloride into one of silver bromide: $AgCl + KBr \rightarrow AgBr + KCl$. This occurs because silver bromide is the less soluble salt. But *free* bromine never displaces chlorine from binary combination with a metallic element. It is free chlorine that displaces combined bromine.

Non-Ionic Modes of Forming Ionogens. — While ionogens may always be made by the union of the proper ions, they must nevertheless, in the absence of the solvent, be regarded as chemical substances which may be constructed, and very frequently are made, out of their constituents without reference to the ionic plane of cleavage. Thus we have incidentally observed many ways in which acids, bases, and salts may be prepared, that do not involve a union of the constituent ions and are probably not ionic.

Oxygen **acids** can almost all be prepared from the **anhydride,** that is, the oxide of the non-metal, which is not an ionogen, and water. Phosphoric acid, sulphurous acid (p. 94), hypochlorous acid ($Cl_2O + H_2O \rightarrow 2HClO$), and many other acids are so formed. Hydrogen fluoride, chloride, bromide, and iodide are all producible by union of the constituent elements. Many acids are formed from others when the latter are decomposed; for example, hydrochloric acid from hypochlorous acid (p. 161).

Bases are formed by the union of oxides of metals with water (p. 94).

The dry ways of forming **salts** are very numerous. Thus, many are produced by direct union of the elements, as in the case of chlorides (p. 146), sulphides (p. 14), and other simple salts. Many are made by reduction or oxidation from other salts, as potassium chloride from potassium chlorate (p. 27), or potassium perchlorate (*q.v.*) from the latter. Often a reducing or an oxidizing agent is used, as in making sodium nitrite (see index) from the nitrate. Almost all oxygen salts can be obtained by the union of two oxides, as calcium carbonate (see index) from calcium oxide and carbon dioxide. Ammonium salts are formed by combination of ammonia, which is not an ionogen, with acids (p. 146).

In **manufacturing** commercially important salts, methods like the above, as well as those involving ionic actions, are very commonly used. In each case the cheapest and most easily accessible materials are chosen, and the least expensive operation is selected.

Exercises. — 1. Give, for each of the following, a definition, *i.e.*, concise description, in terms of experimental facts: acid (pp. 52, 158, 210, 246), base (pp. 94, 146, 246), salt (p. 246), acid salt, mixed salt.

2. Give, now, a definition of the same things (see 1), in terms of ions.

3. Name all the ionic substances whose formulæ are given on pp. 212, 237, and classify them into anions and cations.

4. Give a list of the specific physical and chemical properties, including those that can be used as tests, of: iodide-ion, sulphate-ion, cupric-ion, chloride-ion.

5. Give a list of all the colorless ionic substances you can think of.

6. Using the table of fractions ionized (p. 241), prepare lists of the pairs of ionic substances which show the greatest, and the least tendency to combine, and state in each case the proportion combining in decinormal solution.

7. In the case of the green solution of cupric bromide (p. 249), explain in detail (p. 181) the effect of the addition of potassium bromide. Formulate the action (p. 251).

8. In the case of the chocolate-brown, concentrated solution of cupric bromide (p. 249), explain in detail what would happen to the system: (*a*) if metallic zinc were to be added (p. 259); (*b*) if hydrogen sulphide gas were to be led into the solution (CuS is insoluble).

9. Formulate, after the models on pp. 251 and 252, and discuss fully, the interaction of ferric chloride and ammonium thiocyanate (p. 182).

10. What is implied by the statements, that peroxides are salts and that hydrogen peroxide is feebly acid (p. 223)?

11. Formulate after the model on p. 252, and discuss fully, the interaction of: (*a*) sodium peroxide and hydrochloric acid (p. 222); (*b*) barium peroxide and sulphuric acid.

12. Invent an interaction of two soluble salts in which both products shall be insoluble (see Table of Solubilities, inside of front cover) and formulate it, (p. 252).

13. For the neutralization of 77 c.c. of a certain alkaline solution, 25 c.c. of normal hydrochloric acid are required. What is the normal concentration of the alkali? If the alkali was sodium hydroxide, what weight of the substance was present? If the alkali was barium hydroxide, what weight of it was present?

14. Formulate (p. 259) the actions of iron and of aluminium on dilute hydrochloric acid.

15. Formulate (p. 259) the displacements of iodine by chlorine and by bromine (p. 200).

16. Which metals (p. 260), besides platinum, would be most likely to form suitable electrodes for an electrolytic cell?

17. To which classes of ionic actions do those of iodine on hydrogen sulphide (p. 201), and of calcium on cold water (p. 50), belong?

CHAPTER XX

SULPHUR AND HYDROGEN SULPHIDE

Occurrence. — Free sulphur is found in volcanic regions in Sicily, where it is mixed with gypsum and other minerals and occupies the pores of pumice-stone. Rocky materials accompanying a mineral in this way are called the **matrix.** The other important deposit is in Louisiana. There are many minerals containing sulphur but, with the exception of pyrite, these are chiefly important on account of their other constituents. Sulphides of metals, such as pyrite FeS_2, copper pyrites $CuFeS_2$, galena PbS, zinc-blende ZnS, and sulphates, like gypsum $CaSO_4,2H_2O$, barite $BaSO_4$, and celestite $SrSO_4$, are fairly plentiful. Sulphur is a constituent of the proteins, which are important components of the structure of plants and animals.

Manufacture. — In Sicily, sulphur is obtained by the simple process of melting it away from the accompanying volcanic rock at a low temperature. The liquid sulphur is allowed to run into wooden molds, in which it solidifies in the form of **roll sulphur,** or roll **brimstone.** To produce the best quality it is subjected to distillation from earthenware retorts. When the vapor is led into a large brick chamber, it condenses upon the walls and floor at first in the form of **flowers of sulphur,** and later, when the chamber becomes heated, as a liquid.

In Louisiana, the sulphur forms a deposit over half a mile in diameter, below 900 feet of clay, quicksand, and rock. It is extracted by the Frasch method, by means of borings which permit four pipes, one within the other, to reach the deposit. Water, previously heated under pressure to 170°, is pumped down the two outside pipes (6 and 8 inches in diameter). After time has been allowed for the melting of a mass of the sulphur (m.-p. 114.5°), compressed air is forced down the innermost, one-inch pipe. The melted sulphur has twice the specific gravity of the water in the outer pipes. But the mixture of air and sulphur has about the same specific gravity, and so flows freely up the three-inch pipe surrounding the air pipe. The element flows into a large, wooden enclosure, in which it solidifies, and is practically pure sulphur. Each well, until obstructed by collapse of the rock and quicksand at the bottom, produces 500 tons a day.

The greater part of the sulphur of commerce formerly came from Sicily, where, in 1898, 447,000 tons were manufactured against 41,000 tons elsewhere. The whole supply of the United States (250,000 tons) is now obtained from Louisiana. The world's consumption is over 800,000 tons.

Physical Properties. — The chief physical peculiarity of sulphur is that, instead of appearing in only three familiar physical states, like water, it possesses two familiar and perfectly distinct solid forms and two different liquid states of aggregation.

1. *Rhombic Sulphur.* Native sulphur is yellow, has a sp. gr. 2.06 and melts at 112.8°. It is almost insoluble in water, but dissolves freely in carbon disulphide (41 parts in 100 at 18°). The crystals of native sulphur, as well as those obtained by evaporating a solution, belong to the rhombic system (Fig. 7, p. 12). Roll sulphur and most specimens of flowers of sulphur are the same substance although the crystals in their growth have interfered with one another, and the mass is **crystalline,** simply, and not **well crystallized.** This variety is called, from its form, **rhombic sulphur.** This form is stable below 96°. Above that temperature it changes slowly into monoclinic sulphur.

2. *Monoclinic Sulphur.* When a large mass of melted sulphur solidifies slowly, and the crust is pierced and the remaining liquid poured out before the whole has become solid, the interior is found to be lined with long, transparent needles (Fig. 84). This kind of sulphur is nearly colorless, has a sp. gr. 1.96, melts at 119.25°, and is in all physical respects a different individual from rhombic sulphur. This variety is named, from the system to which its crystals belong, **monoclinic sulphur.** This form can be kept above 96° (transition point, p. 86), but when allowed to cool, it slowly becomes opaque, changing into particles of rhombic sulphur.

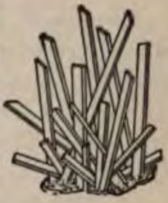

FIG. 84.

A substance which has two solid states of aggregation and, therefore, two crystalline *forms*, is said to be **dimorphous** (two-formed).

3. *S_λ and S_μ, Vapor.* When melted sulphur is heated, it undergoes a gradual change, which is especially noticeable near 160°. The formerly **pale-yellow, mobile liquid** (S_λ) suddenly becomes **dark-brown** in color and so **viscous** (S_μ) that the vessel may be inverted without loss of material: $S_\lambda \rightleftarrows S_\mu$. The liquid is a mixture, containing increasing proportions of S_μ. Beyond 260° the viscidity becomes less, and at 444.7° the liquid boils and passes into sulphur **vapor.**

When ordinary sulphur is raised to the boiling point and then allowed *slowly* to cool, the product is crystalline and soluble in carbon disulphide, as before. The change from S_λ to S_μ is reversible. But when sulphur is boiled and then *suddenly chilled* by pouring into cold water, it is at first semi-fluid. After several days this plastic sulphur, as it is called, becomes hard. It is then found to contain rhombic sulphur mixed with 30 per cent of another variety of free sulphur, namely S_μ. This part is almost insoluble in any solvent. Being without crystalline structure, it is called **amorphous** (Gk., *without form*) **sulphur.** Now amorphous bodies (see Glass) are always supercooled liquids, that is, liquids still existing as such at a temperature at which the solid, crystalline form is the stable one. This is simply the S_μ in a supercooled state. When cold, it reverts very slowly to the soluble variety, and years are required for the completion of the reversion at room temperature.

Chemical Properties. — At low temperatures and under reduced pressure, the formula of sulphur vapor is S_8. As the temperature is raised, however, the vapor expands very rapidly, and at 800° the molecular weight is 64.2, and the formula therefore S_2 (p. 117). The formula of dissolved sulphur, as measured by the freezing-point method (p. 213), is S_8.

Sulphur is an active chemical substance (p. 208). When finely divided *metals*, with the exception of gold and platinum (pp. 60, 260), are rubbed together with powdered sulphur, union takes place and sulphides are produced. Sulphur when heated combines with great vigor with iron (p. 13), copper, and most of the metals. It unites also with many of the *non-metals.* Thus with oxygen it produces sulphur dioxide (p. 31), and even sulphur trioxide SO_3. It unites also with chlorine directly. When sulphur is treated with oxidizing agents *in presence of water*, no trace of sulphur dioxide (or sulphurous acid) is formed; the only product is sulphuric acid (see p. 289).*

Uses of Sulphur. — Large quantities of crude sulphur are employed for making sulphur dioxide, which is used in the manufacture of sulphuric acid, in bleaching feathers, straw, and wool, in preserving dried fruits, and in making alkali sulphites for employment in the bleaching industry and in paper-making. The manufacture of carbon disulphide also consumes much sulphur. Purified sulphur is employed in the manufacture of gunpowder, fireworks, matches, and, by combination with rubber, of vulcanite. Flowers of sulphur is used in vineyards to destroy fungi, which it does by virtue of the traces of sulphuric acid it yields by oxidation.

HYDROGEN SULPHIDE H_2S

This gas is found dissolved in some mineral waters, which in consequence are known as sulphur waters. It is produced in the decomposition of animal matter containing sulphur (proteins), when air is excluded. Hence the odor of rotten eggs is due in part to its presence.

Preparation. — 1. Hydrogen and sulphur do not unite perceptibly in the cold. At 310° almost complete union occurs, but about 168 hours are required for the attainment of equilibrium.

2. Sulphides of metals, being salts, are acted upon more or less easily by dilute acids, and give hydrogen sulphide. Ferrous sulphide, the least expensive of those easily affected, is generally used:

$$FeS + 2\,HCl \leftrightarrows H_2S \uparrow + FeCl_2.$$

For hydrochloric acid we may substitute an aqueous solution of any active, *non-oxidizing* acid (see p. 268, last line). A Kipp's apparatus (p. 54) is commonly employed.

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* The paragraph on the chemical relations of the element (see end of this chapter) should be read at this point.

3. Hydrogen sulphide is the invariable product of the extreme reduction of any sulphur compound. Thus, it is formed by the action of hydrogen iodide upon concentrated sulphuric acid (p. 201). Even sulphur itself is reduced by dry, gaseous hydrogen iodide:

$$2HI + S \rightarrow H_2S + I_2.$$

Physical Properties. — Hydrogen sulphide is a colorless gas with a characteristic odor. When liquefied, it boils at −62°, and in solid form melts at −83°. The solubility in water at 10° is 360 volumes in 100, and becomes less as the temperature is raised. The gas can be driven out completely by boiling the solution (*cf.* p. 145). The gas is very poisonous, one part in two hundred of air being fatal to mammals.

Chemical Properties of Hydrogen Sulphide Gas. — When heated, the gas **dissociates**:

$$H_2S \rightleftarrows H_2 + S.$$

At 310° the decomposition is slight (*cf.* p. 267), but becomes greater at higher temperatures.

The gas **burns** in air, forming steam and sulphur dioxide. The temperature of the mantle of flame surrounding the gas, as it issues from a jet, being far above 310°, the gas in the interior is dissociated *before* it meets with any oxygen. Hence a *cold* dish held across the flame (Fig. 85) receives a deposit of free sulphur, and a part of the hydrogen also escapes unburnt. It may be remarked that dissociation of this kind probably precedes the combustion of most gaseous compounds (see Flame).

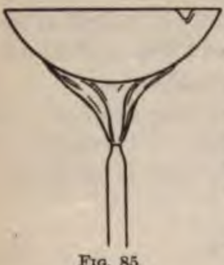

FIG. 85.

The metals, down to and including silver in the electromotive series, when exposed to the gas, quickly receive a coating of sulphide. The tarnishing of silver in the household is probably due to a trace of hydrogen sulphide in the illuminating gas which escapes from slight leaks in the pipes. That the gas should thus behave like free sulphur shows its **instability**.

This instability is shown also in the fact that it **reduces** substances, such as sulphur dioxide, which are not affected by free hydrogen:

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S.$$

This action takes place in the cold, and much more rapidly when the gases are moist than when they are dry (p. 160). Some native sulphur is produced by this action, but usually it arises from the reduction of gypsum $CaSO_4,2H_2O$ to CaS, and liberation from the sulphide. Sulphur is deposited also when hydrogen sulphide undergoes a partial combustion with a restricted supply of oxygen, $2H_2S + O_2 \rightarrow 2H_2O + 2S$, and its formation in nature is sometimes to be accounted for in this way.

A Characteristic of Reduction and Oxidation. — In the former of the two actions last mentioned, it will be seen that, while the SO_2 was reduced to S, at the same time H_2S was *oxidized* (to S). In the second action, H_2S was oxidized to S, and O_2 was *reduced* to $2H_2O$. It is a characteristic of such actions that one substance is oxidized and another reduced: oxidation and reduction always occur together, in the same reaction. Here, under hydrogen sulphide, we speak of its *reducing* effect on sulphur dioxide. Under sulphur dioxide, however, we should speak of the oxidizing effect of the substance on hydrogen sulphide.

Chemical Properties of the Aqueous Solution of Hydrogen Sulphide. — While the gas itself is not an acid, its solution in water gives a **feeble acid reaction** with litmus, and is sometimes named **hydrosulphuric acid** H_2S, Aq. The conductivity of a $N/10$ aqueous solution is small, and only 0.0007 (0.07 per cent) of the substance is ionized:

$$H_2S \leftrightarrows H^+ + HS^- \ (\rightleftarrows H^+ + S^=).$$

Some $S^=$ ions are present. But hydrosulphide-ion HS^-, although an acid, is less dissociated than is water itself, and the amount of sulphide-ion is therefore very small. The salts of hydrosulphide-ion, such as NaHS (sodium acid sulphide, see next section), give therefore neutral solutions. This behavior is the rule with the acid salts of feeble dibasic acids (p. 241).

As an acid, the solution of hydrogen sulphide may be neutralized by bases. For the same reason it enters into double decomposition with salts (see next section).

By the action of **oxygen** from the air upon an aqueous solution of hydrogen sulphide, the **sulphur is** slowly **displaced** and appears in the form of a fine white powder:

$$O_2 + 2H_2S \rightarrow 2S\downarrow + 2H_2O.$$

This is an action similar to the displacement of ionic bromine by free chlorine (p. 259).

The solution of the gas is a **reducing agent,** as its action upon iodine shows (p. 202). So, also, in presence of an acid, it removes oxygen from dichromic acid (produced by the action of an acid upon potassium dichromate):

$$\begin{array}{lr} K_2Cr_2O_7 + 2HCl \rightleftarrows H_2Cr_2O_7 + 2KCl. & (1) \\ H_2Cr_2O_7 + 6HCl \rightarrow 4H_2O + 2CrCl_3\ (+ 3O). & (2) \\ (3O) + 3H_2S \rightarrow 3H_2O + 3S. & (3) \\ \hline \text{Adding: } K_2Cr_2O_7 + 8HCl + 3H_2S \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3S. & \end{array}$$

The first partial equation (*cf.* p. 194) represents the regular interaction of two ionogens, but the second interaction does not take place unless an oxidizable body (here the hydrogen sulphide) is present to take possession of the oxygen which it is capable of delivering (*cf.* p. 225).

The foregoing illustrates a **fourth kind of ionic chemical change** (p. 259), namely that in which **a compound ion is formed or decomposed.** Here dichromate-ion $Cr_2O_7^{=}$ gives chromic-ion Cr^{+++} and water. For other illustrations see pp. 56, 161, 206, 224, 225, 274.

Sulphides. — As a dibasic acid (p. 269), hydrogen sulphide gives both acid and normal (or "neutral") sulphides, such as NaHS and Na_2S.

The **acid sulphides** are obtained by passing the gas *in excess* into solutions of soluble bases:

$$H_2S + NaOH \rightarrow H_2O + NaHS,$$

and are *neutral* in reaction. Their negative ion, HS^{-}, is not further dissociated (see preceding section).

By adding to the above-mentioned solution an amount of sodium hydroxide equal to that used before, and driving off the water by evaporation, the second unit of hydrogen is displaced, and normal ("neutral") sodium sulphide is formed:

$$NaOH + NaHS \leftrightarrows Na_2S + H_2O \uparrow.$$

This action is wholly reversed when the dry sodium sulphide is dissolved in water, the salt being completely **hydrolyzed** (p. 197) to the acid salt:

$$\left.\begin{array}{l} Na_2S \leftrightarrows 2Na^+ + S^= \\ H_2O \leftrightarrows OH^- \;\; + H^+ \end{array}\right\} \leftrightarrows HS^-.$$

The HS^- gives a lower concentration of hydrogen-ion than the water, and hence uses up in its formation the ions of hydrogen produced by the latter, until an amount of hydroxide-ion equivalent to half the sodium is formed. The abbreviated equation shows this more clearly:

$$S^= + H^+ + OH^- \rightarrow HS^- + OH^-.$$

The solution is therefore strongly alkaline in reaction. **In general, a normal salt derived from an active base and a weak acid is hydrolyzed** to some extent **by water** and gives an **alkaline solution.**

In the abbreviated formulation used above, the union of Na^+ and OH^- to form NaOH is not shown, because it is slight in dilute solution and does not affect the result. The union of $S^=$ and H^+ to form HS^- is alone shown, because it is extensive and significant. To save space, this plan will be used in future, where the same situation exists.

The soluble acid sulphides are **oxidized** in aqueous solution by atmospheric oxygen:

$$2NaSH + O_2 \rightarrow 2NaOH + 2S.$$

The sulphur is not precipitated, but combines with the excess of the sulphide, forming polysulphides (see below). Some sodium thiosulphate is produced at the same time.

The Action of Acids on Insoluble Sulphides. — The interaction of sulphides and acids is itself so important a matter in chemistry, and is so similar in theory to many other kinds of actions, that special attention should be given to it. The common method of preparing hydrogen sulphide from ferrous sulphide affords a suitable illustration.

Since ferrous sulphide is but slightly soluble in water, the action proceeds by a rather complex series of equilibria:

$$\left.\begin{array}{r} FeS\ (solid) \leftrightarrows FeS\ (dslvd) \leftrightarrows Fe^{++} + S^{=} \\ 2HCl \leftrightarrows 2Cl^{-} + 2H^{+} \end{array}\right\} \leftrightarrows H_2S\ (dslvd) \rightleftarrows H_2S\ (gas).$$

It will be seen that a number of reversible changes are involved, and the question is, why does the reaction proceed forward, as it does? To answer this question, a consideration of each of the equilibria, separately, is required.

1. The dissolved hydrogen sulphide is very feebly ionized, and maintains a smaller concentration of sulphide-ion $S^{=}$ than does ferrous sulphide, in spite of the comparative insolubility of the latter. Hence, the $S^{=}$ formed from the FeS is continuously removed by union with the hydrogen-ion furnished by the acid, $S^{=} + 2H^{+} \leftrightarrows H_2S$, and all the other equilibria are constantly displaced forward on this account. The action is therefore, in essence, like neutralization (p. 254).

2. The union of $S^{=}$ and $2H^{+}$ depends on the magnitude of the *product* of their concentrations (p. 184), $[S^{=}] \times [H^{+}] \times [H^{+}]$, or $[S^{=}] \times [H^{+}]^2$. Hence, although $[S^{=}]$ is minute, on account of the insolubility of FeS, $[H^{+}]$ is large on account of the great dissociation of the HCl and the fact that a strong solution of the acid can be used. Thus the *product* may be large enough for the purpose.

3. When a still more insoluble sulphide, like cupric sulphide CuS is employed, the concentration of the sulphide-ion $[S^{=}]$ is too small to play its part and the action makes almost no progress. In this case, a concentration of H^{+}, sufficient to raise the product to the necessary value, cannot be obtained with any acid.

4. The fact that hydrogen sulphide is fairly soluble (3.6 vols. : 1 vol.) *hinders* the action. It prevents that free escape of one product which is so constantly a factor in promoting reversible chemical changes. Thus, if cadmium sulphide CdS, which lies between ferrous and cupric sulphides, in solubility, is employed along with rather dilute hydrochloric acid, a concentration of hydrogen sulphide sufficient to stop the action accumulates before the liquid is saturated with the gas, and the latter can begin to escape. There are then two ways of making this action continuous. Either stronger hydrochloric acid, giving a higher concentration of H^{+} may be used to force the formation of more H_2S (by union of $2H^{+}$

and $S^=$), or the reverse action, due to accumulation of H_2S (dslvd), may be diminished mechanically by leading air through the mixture (p. 129) and so removing the hydrogen sulphide as fast as it is formed. Either plan will cause complete interaction with the cadmium sulphide.

Classification of Insoluble Sulphides. — In analytical chemistry, advantage is taken of the different solubilities of the sulphides, for the purpose of identifying the metallic elements, and of separating mixtures containing several such elements. Three classes are distinguished.

1. The sulphides of silver, copper, mercury, and some other metals are exceedingly insoluble, and, therefore, do not interact with dilute acids as does ferrous sulphide (p. 271). These may therefore be made by leading hydrogen sulphide into solutions of their salts:

$$CuSO_4 + H_2S \leftrightarrows CuS\downarrow + H_2SO_4.$$

The acid produced has scarcely any effect upon the sulphide, and almost no reverse action is observed. In this action the sulphide-ion is the active substance and, by its removal, all the equilibria are displaced forwards.

2. The sulphides of iron, zinc, and certain other metals are insoluble in water, but not so much so as the last class. Hence they are decomposed by dilute acids, and the reverse of the above action takes place almost completely. These sulphides must therefore be made, either by combination of the elements, or by adding a soluble sulphide to a solution of a salt:

$$FeSO_4 + (NH_4)_2S \leftrightarrows FeS\downarrow + (NH_4)_2SO_4.$$

No acid is produced in this sort of interaction, and the considerable insolubility of the sulphide of iron or zinc in water renders the change nearly complete.

3. The sulphides of barium, calcium, and some other metals (*q.v.*), although insoluble in water, are hydrolyzed by it, and give soluble products, the hydroxide and hydrosulphide:

$$2CaS + 2H_2O \leftrightarrows Ca(OH)_2 + Ca(SH)_2.$$

They may be prepared by direct union of the elements, and from the sulphates by reduction with carbon. But they are not precipitated by hydrogen sulphide or ammonium sulphide.

Polysulphides. — When sulphur is shaken with a solution of a soluble sulphide or acid sulphide, such as sodium sulphide, it dissolves, and evaporation of the solution leaves residues, varying in composition from Na_2S_2 to Na_2S_5. These appear to be mixtures composed mainly of Na_2S and Na_2S_4.

When an acid is poured into sodium polysulphide solution, minute spherules of rhombic sulphur are precipitated:

$$Na_2S_4 + 2HCl \rightarrow 2NaCl + H_2S\uparrow + 3S\downarrow.$$

The Chemical Relations of the Element Sulphur. — In combination with metals and hydrogen, sulphur is bivalent, forming compounds like H_2S, FeS, CuS, and HgS. In combination with non-metals, however, the valence is frequently greater, the maximum being seen in sulphur trioxide, where the sulphur is sexivalent. Its oxides are acid-forming, and it is, therefore, a non-metal.

Exercises. — 1. How could the decomposition of hydrogen sulphide at 310° be rendered, (*a*) more complete, (*b*) less complete? Would the percentage decomposed be affected, (*a*) by reducing the pressure, (*b*) by mixing the gas with an indifferent gas?

2. What are the relative volumes of the gases (p. 150) in the action of, (*a*) hydrogen iodide and sulphur, (*b*) hydrogen sulphide and sulphur dioxide?

3. To what classes of ionic actions (p. 259) do the interactions of hydrogen sulphide solution with, (*a*) oxygen (p. 270), (*b*) sodium hydroxide (p. 270), (*c*) iodine (p. 202) belong?

4. Show which actions on the pages referred to on p. 270 illustrate the fourth kind of ionic chemical change, and how they do so?

5. Why is normal sodium sulphide only half hydrolyzed by water?

6. Formulate completely, after the model on p. 252, the actions of (*a*) hydrogen sulphide and cupric sulphate solution; (*b*) ammonium sulphide and ferrous sulphate. In each case explain which equilibrium determines the direction of the action.

CHAPTER XXI

THE OXIDES AND OXYGEN ACIDS OF SULPHUR

THE only important oxides of sulphur are the **dioxide** SO_2 and the **trioxide** SO_3. They are the anhydrides (p. 94) of sulphurous acid H_2SO_3 and of sulphuric acid H_2SO_4, respectively.

The Preparation of Sulphur Dioxide SO_2. — 1. When sulphur burns in air or oxygen, sulphur dioxide is produced (p. 32). 2. The larger part of the sulphur dioxide used in commerce is probably obtained by the **roasting** (**calcining**) of sulphur ores. Pyrite FeS_2, for example, on account of the large amount of sulphur which it contains, can be burnt in a suitable furnace:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2\uparrow.$$

The gas, although mixed with great amount of nitrogen which entered as part of the air, can be used to make sulphuric acid.

It should be noted, in passing, that heating and roasting or calcining are distinct processes in chemistry. **Roasting** or **calcining** always assumes the access of the air and employment of its oxygen; **heating**, in the absence of modifying words, assumes the exclusion or the chemical indifference of the air.

3. In the laboratory, a steady stream of the gas is obtained by allowing hydrochloric acid to drop upon solid sodium acid sulphite, or concentrated sulphuric acid to trickle into a 40 per cent solution of the same salt (Fig. 24, p. 54):

$$HCl + NaHSO_3 \leftrightarrows NaCl + H_2SO_3 \leftrightarrows H_2O + SO_2\uparrow.$$

The sulphurous acid, being very unstable, decomposes spontaneously into water and sulphur dioxide, and the latter escapes when sufficient water for its solution is not present.

4. Sulphur dioxide can also be made by the reduction of concentrated sulphuric acid by copper at a high temperature. A part

of the acid loses oxygen to form water with the hydrogen of another molecule:

Partial 1: $H_2SO_4 \rightarrow H_2O + SO_2\ (+\ O).$

Partial 2: $\underline{(O) + H_2SO_4 + Cu \rightarrow H_2O + CuSO_4.\qquad}$

$$2H_2SO_4 + Cu \rightarrow 2H_2O + SO_2 + CuSO_4.$$

Some easily oxidized non-metals, such as carbon and sulphur, act in the same way, $C + 2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + CO_2$.

Making Equations by Positive and Negative Valences. — Equations like the foregoing can be constructed also by assuming that each element in a compound is either positive or negative, and by marking the valences accordingly (for details, see p. 322). Thus, in sulphuric acid, we have $2H^+$ (positive, univalent) and $4O^=$ (each bivalent and negative). Since the numbers of positive and negative valences must be equal, and we have $2\oplus$* and $8\ominus$, it follows that the sulphur carries $6\oplus$, S^{++++++}.

Now when, in making the experiment, we find the products SO_2 and $CuSO_4$, we may infer that the hydrogen formed water. We infer, also, that to obtain *two* compounds containing sulphur, at least $2H_2SO_4$ was required. We then note that the S in SO_2 is quadrivalent. Hence S^{++++++} became S^{++++} and $2\oplus$ were released. The metallic copper used was free and without valence, and became $CuSO_4$, in which it is Cu^{++}. It obtained the $2\oplus$ from the sulphur. The action can therefore be analyzed as follows:

$$\underset{\text{First } H_2SO_4}{[2H^+ + S^{++++++} + 4O^=]} \rightarrow \underset{SO_2}{[S^{++++} + 2O^=]} + \underset{H_2O}{[2H^+ + O^=]} + \underset{\text{Balance}}{[O^= + 2\oplus]}$$

The second H_2SO_4 gives $[2H^+ + SO_4^=]$. The Cu takes the $2\oplus$ giving Cu^{++}, and this with the $SO_4^=$ gives $CuSO_4$. The $2H^+$ takes the $O^=$ from the balance, giving H_2O. Thus, the whole balance is used and the products are accounted for. The equation must therefore be:

$$2H_2SO_4 + Cu \rightarrow SO_2 + 2H_2O + CuSO_4.$$

It will be noted that the two molecules of sulphuric acid play different rôles. Only one of them is used in oxidizing.

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* The signs $\oplus$ and $\ominus$ stand for quantities of electricity equal to those carried by one equivalent of an ionic substance, and therefore required for its discharge and liberation.

Similarly, with sulphuric acid and carbon, the same analyzed equation applies. The carbon gives CO_2. Thus, the carbon goes from C^0 to $C^{\ddagger\ddagger}$. To obtain the $4\oplus$, $2H_2SO_4$ is required (equation above). Hence,

$$2H_2SO_4 + C \rightarrow CO_2 + 2SO_2 + 2H_2O.$$

When hydrogen sulphide is led through concentrated sulphuric acid, the latter is reduced to sulphur dioxide, and the former is oxidized, giving free sulphur (p. 270):

$$2H^+ + S^= + 2\oplus \rightarrow 2H^+ + S^0\downarrow.$$

Since this action requires $2\oplus$, and sulphuric acid in giving SO_2 delivers $2\oplus$, it follows that $1H_2SO_4$ will decompose $1H_2S$:

$$H_2SO_4 + H_2S \rightarrow 2H_2O + S^0\downarrow + SO_2.$$

Finally, when HI with sulphuric acid (p. 201) gives free iodine (I^0), and H_2S ($2H^+ + S^=$), evidently $S^{\ddagger\ddagger\ddagger}$ in sulphuric acid gives up $8\oplus$, becoming $S^=$:

$$[2H^+ + S^{\ddagger\ddagger\ddagger} + 4O^=] \rightarrow 2H^+ + S^= + 4O^= + 8\oplus$$

and $$[H^+ + I^-] + \oplus \rightarrow H^+ + I^0.$$

Evidently, $1H_2SO_4$ giving $8\oplus$ will interact with 8HI, changing $8I^-$ into $8I^0$. Hence,

$$H_2SO_4 + 8HI \rightarrow 4H_2O + H_2S + 8I^0.$$

The reader should practice the use of this method by making the equations for the actions of zinc (p. 268 giving hydrogen sulphide) and of hydrogen bromide (p. 196) upon sulphuric acid.

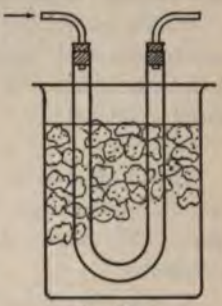

Fig. 86.

Physical and Chemical Properties. — Sulphur dioxide is a gas possessing a penetrating and characteristic *odor*. This is frequently spoken of as the "odor of sulphur," but it should be remembered that sulphur itself has scarcely any smell at all. The weight of the G.M.V. of the gas (65.54 g.) shows it to be more than *twice as heavy as air*. By means of a freezing mixture of ice and salt (Fig. 86), the gas is easily condensed in a U-tube to a transparent mobile *fluid*, which boils at −8°. At 20°, the liquid gives a vapor pressure of only $3\frac{1}{4}$ atmospheres, so that the liquid is handled and sold in glass syphons or in sealed tin cans. The *solubility* of the gas in water is 5000 volumes in 100. The liquid is completely freed from the gas by boiling (*cf.* p. 145).

As regards **chemical properties,** sulphur dioxide is **stable** (p. 93). It **unites with water** to form sulphurous acid H_2SO_3, which is unstable, and exists only in solution.

Since the maximum valence of sulphur is 6, sulphur dioxide, in which but four of the valences of sulphur are used, is **unsaturated.** It is therefore still able to combine directly with suitable elements, such as chlorine and oxygen. When it is mixed with chlorine in sunlight, a liquid, **sulphuryl chloride** SO_2Cl_2 is produced.

Liquefied sulphur dioxide is employed for bleaching straw, wool, and silk (see p. 289). As a disinfectant it has been displaced to a large extent by formaldehyde.

The Liquefiability of Gases. — It will assist us in recalling which gases are hard to liquefy and which easy, if we memorize the fact that Faraday (from 1823 to 1845) liquefied most of the familiar gases and failed only with three, namely **hydrogen** (c.t. −242°), **oxygen** (c.t. −113°), and **nitrogen** (c.t. −146°). These, with **nitric oxide** NO (c.t. −93.5°), **carbon monoxide** CO (c.t. −40°), **methane** CH_4 (c.t. −99°), and the six **inert gases** (pp. 335–337), are the ones which have low critical temperatures (*cf.* p. 78) and are **difficult to liquefy.**

Of the gases we have studied, the ones which are more or less **easily liquefied** are: **hydrogen chloride** (c.t. +52°), **bromide,** and **iodide, chlorine** (c.t. +141°), **ozone, hydrogen sulphide** (c.t. + 100°), **sulphur dioxide** (c.t. +154°).

The Solubilities of Gases. — For the purpose of remembering the solubilities of gases in water, it is convenient to divide the gases into **three classes.** The following are the ones we have studied:

1. *Slightly soluble:* Oxygen (4 vol. : 100 at 0°), hydrogen (2 : 100 at 0°).
2. *Soluble:* Chlorine (260 vol. : 100 at 10°), hydrogen sulphide (440 : 100 at 0°).

3. *Very soluble:* Hydrogen chloride (505 vol. : 1 at 0°), bromide (404 : 1) and iodide (1570 : 1), sulphur dioxide (69 : 1 at 0°).

Preparation of Sulphur Trioxide SO_3. — Although the formation of sulphur trioxide is accompanied by the liberation of much heat, sulphur dioxide and oxygen, whether cold or warm, unite very slowly. Ozone, however, combines with the former readily.

The interaction of sulphur dioxide and oxygen is hastened by finely divided platinum, which remains itself unchanged and simply acts as a catalytic agent. The **contact process,** as this is called, has been rendered available for the commercial manufacture of sulphur trioxide by Knietsch (1901). At 400°, the temperature used, 98–99 per cent of the materials unite.

$$O_2 + 2SO_2 \rightarrow 2SO_3 + 2 \times 22{,}600 \text{ cal.}$$

Below 400°, the union is too slow. Above 400°, the reverse action is strengthened (Van't Hoff's law, p. 188), and the union is too incomplete. The vaporous product is condensed by being led into 97–99 per cent sulphuric acid, and the concentration of the liquid is constantly maintained at this point by the regulated influx of water. The sulphur dioxide is obtained by calcining ores (p. 275). These contain impurities which must be removed very thoroughly. Dust from the roasting and oxide of arsenic, which are present, will otherwise "poison" the contact agent (platinum or ferric oxide) and soon almost stop the union.

The process may be illustrated by placing some platinized asbestos* in a tube (Fig. 66, p. 156), which is gently warmed, and introducing oxygen and sulphur dioxide through the limbs of the Y-tube. Dense fumes appear at the exit (see next section).

Formerly sulphur trioxide was obtained by the distillation of impure ferric sulphate, $Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$.

Physical and Chemical Properties. — Sulphur trioxide is a volatile liquid (b.-p. 46°). The crystals, obtained by cooling, melt at 14.8°. It fumes strongly when exposed to the air, in consequence of the union of the vapor with moisture and the production of minute drops of sulphuric acid. A white crystalline variety, closely resembling asbestos in appearance, is the more familiar form of the substance, which is dimorphous (p. 266).

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* Asbestos, dipped in a solution of chloroplatinic acid and heated in the Bunsen flame: $H_2PtCl_6 \rightarrow Pt + 2HCl\uparrow + 2Cl_2\uparrow$.

As to **chemical properties,** the vapor of sulphur trioxide **dissociates** into sulphur dioxide and oxygen (400°, 2%; 700°, 40%).

Sulphur trioxide is not itself an acid, but it is the **anhydride** of sulphuric acid. When placed in water it unites vigorously, causing a hissing noise due to the steam produced by the heat of the union.

Just as sulphur trioxide unites with water to give hydrogen sulphate, so it **combines** vigorously **with** many **oxides of metals,** producing the corresponding sulphates:

$$H_2O + SO_3 \leftrightarrows H_2SO_4, \qquad CaO + SO_3 \rightarrow CaSO_4.$$

The union of an oxide of a non-metal with the oxide of a metal, in this fashion, is a general method of obtaining salts (*cf.* p. 261).

Oxygen Acids of Sulphur. — Sulphurous and sulphuric acids have been mentioned frequently already. Next to them in importance come thiosulphuric acid and persulphuric acid. The compositions of the acids show their relationships:

Hyposulphur*ous* acid,	$H_2S_2O_4$.	Sodium hyposulph*ite*,	$Na_2S_2O_4$.
Sulphur*ous* acid,	H_2SO_3.	Sodium sulph*ite*,	Na_2SO_3.
Sulphur*ic* acid,	H_2SO_4.	Sodium sulph*ate*,	Na_2SO_4.
Thiosulphur*ic* acid,	$H_2S_2O_3$.	Sodium thiosulph*ate*,	$Na_2S_2O_3$.
Persulphur*ic* acid,	$H_2S_2O_8$.	Sodium persulph*ate*,	$Na_2S_2O_8$.

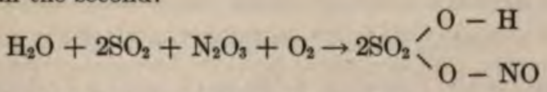
Thiosulphuric acid (Gk. *θεῖον*, sulphur) is so named because it contains one unit of sulphur in place of one of the units of oxygen of sulphuric acid. Note that when the names of the acids end in *ous* and *ic*, the names of the salts end in *ite* and *ate*, respectively. Besides the above we have also the polythionic acids, namely: dithionic acid $H_2S_2O_6$, trithionic acid $H_2S_3O_6$, tetrathionic acid $H_2S_4O_6$, and pentathionic acid $H_2S_5O_6$.

SULPHURIC ACID H_2SO_4

Although salts of sulphuric acid, such as calcium sulphate $CaSO_4$, are exceedingly plentiful in nature, the preparation of the acid by chemical action upon the salts is not practicable. The sulphates, indeed, interact with all acids, but the actions are reversible. The completion of the action by the plan used in making hydrogen chloride (p. 142), involving the removal of the sulphuric acid by distillation, would be difficult on account of the involatility of this acid. It boils at 330°; and suitable acids, less volatile still, which might be used to liberate it, do not exist. We are therefore compelled to build up sulphuric acid from its elements.

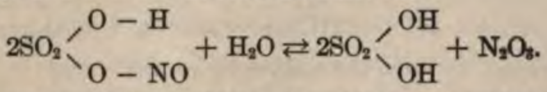
The union of sulphur dioxide and oxygen by the contact process, and combination of the trioxide with water (p. 279), is the best method for making a highly concentrated acid. For obtaining ordinary "oil of vitriol," however, the "chamber process" is still used extensively.

Chemistry of the Chamber Process. — The gases, the interactions of which result in the formation of sulphuric acid, are: water vapor, sulphur dioxide, nitrous anhydride N_2O_3[*] (see index), and oxygen. These are obtained, the first by injection of steam, the second usually by the burning of pyrite, the third from nitric acid HNO_3, and the fourth by the introduction of air. The gases are thoroughly mixed in large leaden chambers, and the sulphuric acid forms droplets which fall to the floors. In spite of elaborate investigations, instigated by the extensive scale upon which the manufacture is carried on and the immense financial interests involved, some uncertainty still exists in regard to the precise nature of the chemical changes which take place. According to Lunge, supporting the view first suggested by Berzelius, the greater part of the product is formed by two successive actions, the first of which yields a complex compound that is decomposed by excess of water in the second:



$$H_2O + 2SO_2 + N_2O_3 + O_2 \rightarrow 2SO_2\left\langle\begin{matrix}O-H\\O-NO\end{matrix}\right. \qquad (1)$$

The group $-NO$, nitrosyl, is found in many compounds. Here, if it were displaced by hydrogen, sulphuric acid would result. Hence this compound is called **nitrosylsulphuric acid**:



$$2SO_2\left\langle\begin{matrix}O-H\\O-NO\end{matrix}\right. + H_2O \rightleftarrows 2SO_2\left\langle\begin{matrix}OH\\OH\end{matrix}\right. + N_2O_3. \qquad (2)$$

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[*] This gas is unstable, breaking up in part into nitric oxide NO and nitrogen tetroxide NO_2: $N_2O_3 \rightleftarrows NO + NO_2$. In this process, however, the mixture behaves as if it were all N_2O_3, and so only nitrous anhydride is named in this connection.

The equations (1) and (2) are not partial equations for one interaction, but represent distinct actions which can be carried out separately. In a properly operating plant, indeed, the nitrosylsulphuric acid is not observed. But when the supply of water is deficient, white "chamber crystals," consisting of this substance, collect on the walls.

The explanation of the success of this seemingly roundabout method of getting sulphuric acid is as follows: The direct union of sulphur dioxide and water to form sulphurous acid is rapid, but the action of free oxygen upon the latter, $2H_2SO_3 + O_2 \rightarrow 2H_2SO_4$, is exceedingly slow. Reaching sulphuric acid by the use of these two changes, although they constitute a direct route to the result, is not feasible in practice. On the other hand, both of the above actions, (1) and (2), happen to be much more speedy, and so, by their use, more rapid production of the desired substance is secured at the expense of a slight complexity.

The progress of the first action is marked by the disappearance of the brown nitrous anhydride and, on the introduction of water, the completion of the second stage results in the reproduction of the same substance. The nitrous anhydride takes part a large number of times in these changes, and so facilitates the conversion of a great amount of sulphur dioxide, oxygen, and water into sulphuric acid, without much diminution of its quantity. Some is lost, however.

The loss of nitrous anhydride is made good by the introduction of nitric acid vapor into the chamber. This acid is made from concentrated sulphuric acid and commercial sodium nitrate $NaNO_3$:

$$NaNO_3 + H_2SO_4 \rightleftarrows HNO_3\uparrow + NaHSO_4.$$

On account of the volatility of the nitric acid, a moderate heat is sufficient to remove it from admixture with the other substances, and its vapor is swept along with the other gases into the apparatus. The initial action which the nitric acid undergoes:

$$H_2O + 2SO_2 + 2HNO_3 \rightarrow 2H_2SO_4 + N_2O_3,$$

may be written, to show the anhydride of nitric acid:

$$H_2O + 2SO_2 + H_2O,N_2O_5 \rightarrow 2H_2SO_4 + N_2O_3.$$

The two molecules of water, one actually, the other potentially, present, with the two molecules of sulphur dioxide, can furnish two molecules of sulphurous acid (H_2SO_3). The N_2O_5 in passing to the condition N_2O_3 gives up the two units of oxygen required to convert this sulphurous acid into sulphuric acid.

Details of the Chamber Process. — The sulphur dioxide is produced in a row of furnaces *A* (Fig. 87). When good pyrite is used, the ore burns unassisted (p. 275), while impure pyrite and zinc-blende ZnS have to be heated artificially to maintain the combustion. The gases from the various furnaces pass into one long dust-flue, in which they are mingled with the proper proportion of air, and deposit oxides of iron and of arsenic, and other materials which they transport mechanically. From this flue they enter the Glover tower *G*, in which they acquire the oxides of nitrogen. Having secured all the necessary constituents, excepting water, the gases next enter the first of the lead chambers, large structures lined completely with sheet lead. These measure as much as 100 × 40 × 40 feet, and have a total capacity of 150,000 to 200,000 cubic feet. As the gases drift through these chambers they are thoroughly mixed, and an amount of water considerably in excess of that actually required is injected in the form of steam at various points. The acid, along with the excess of water, condenses and

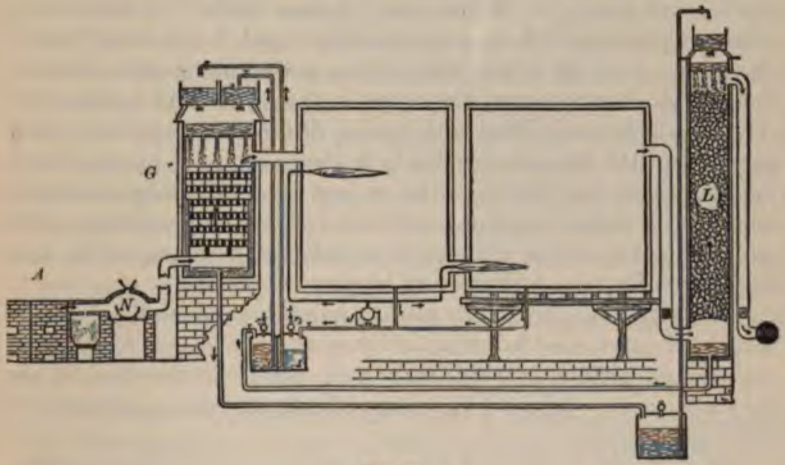

FIG. 87.

collects upon the floor of the chamber, while the unused gases, chiefly nitrous anhydride and nitrogen, the latter derived from the air originally admitted, find an exit into the Gay-Lussac tower *L*.

This is a tower about fifty feet in height, filled with tiles, over which concentrated sulphuric acid continually trickles. The object of this tower, to catch the nitrous anhydride and enable it to be reëmployed in the process, is accomplished by a reversal of action (2) above. The acid which accumulates in the vessel at the bottom of this tower contains the nitrosylsulphuric acid, and by means of compressed air is forced through a pipe up to a vessel at the top of the Glover tower *G*. When this "nitrous vitriol" is mixed with dilute sulphuric acid from a neighboring vessel, by allowing both to flow down into the tower, the nitrous anhydride is once more set free by the interaction of the water in the dilute acid (action (2)). The Glover tower is filled with broken flint or tiles, and the heated gases from the furnace acquire in it their supply of nitrous anhydride. Their high temperature causes a considerable concentration of the diluted sulphuric acid as it trickles downward. The acid, after traversing this tower, is sufficiently strong to be used once more for the absorption of nitrous anhydride.

To replace the part of the nitrous anhydride which is inevitably lost, fresh nitric acid is furnished by small open vessels *N*, containing sodium nitrate and sulphuric acid, placed in the flues of the pyrite-burners. About 4 kg. of the nitrate are consumed for every 100 kg. of sulphur.

The acid which accumulates upon the floors contains but 60 to 70 per cent of sulphuric acid, and has a specific gravity of 1.5–1.62. The excess of water is needed to facilitate the second action. It is required also in order that the acid upon the floor may not afterwards absorb and retain the nitrous anhydride, for this substance combines with an acid containing more than 70 per cent of hydrogen sulphate.

This crude sulphuric acid is applicable directly in some chemical manufactures, such as the preparation of superphosphates (*q.v.*). Concentration is effected by evaporation in pans lined with lead, which are frequently placed over the pyrite-burners in order to economize fuel. The evaporation in lead is carried on until a specific gravity 1.7, corresponding to 77 per cent concentration, is reached. Up to this point the sulphate of lead formed by the action of the sulphuric acid produces a crust which protects the metal from further action. When a stronger acid is required, the water is driven out by heating the sulphuric acid in vessels of glass or platinum, or even of cast iron. Iron acts upon dilute sulphuric acid, displacing the hydrogen-ion, but not upon concentrated sulphuric acid, which is not ionized. Commercial sulphuric acid, **oil of vitriol,** has a specific gravity 1.83–1.84, and contains about 93.5 per cent of hydrogen sulphate.

Physical Properties. — Pure hydrogen sulphate has a sp. gr. 1.85 at 15°. When cooled, it crystallizes (m.-p. 10.5°). At 150°–180° the acid begins to fume, giving off sulphur trioxide. It boils at 330°, but loses more sulphur trioxide than water and finally yields an acid of constant (p. 145) boiling-point (338°) and constant composition (98.33 per cent). The heat of solution (p. 125) of hydrogen sulphate is very great (39,170 cal.). The solution is thus much more stable (*i.e.*, it contains much less energy) than the pure substance, and hence the latter absorbs water greedily.

Commercial sulphuric acid is **impure.** It contains, for example, lead sulphate, which appears as a precipitate when the acid is diluted, as well as arsenic trioxide and oxides of nitrogen in combination.

Chemical Properties and Uses of Hydrogen Sulphate. — 1. The compound is **not** exceedingly **stable,** for dissociation into water and sulphur trioxide begins far below the boiling-point. The vapor of the acid boiling at 338° contains 30 per cent of $H_2O + SO_3$, which recombine when the vapor is condensed. The dissociation is practically complete at 416°, as is shown by the density of the vapor. When raised suddenly to a red heat it is broken up completely into water, sulphur dioxide, and oxygen.

2. When sulphur trioxide is dissolved in hydrogen sulphate, **disulphuric acid** $H_2S_2O_7$, a solid compound, is obtained. Hydrogen sulphate containing 80 per cent of disulphuric acid is known as "oleum," and is employed in chemical industries. The salts of disulphuric acid may be made by strongly heating the acid sulphates, for example:

$$2NaHSO_4 \rightleftarrows Na_2S_2O_7 + H_2O\uparrow.$$

In view of this mode of preparation by the aid of heat, they are frequently known as **pyrosulphates** (Gk. πῦρ, fire). When they are dissolved in water, the acid sulphates are reproduced.

3. With salts which it does not oxidize (see below), hydrogen sulphate **reacts by double decomposition** and sets free the corresponding acid. Where the new acid is volatile, as in the case of hydrogen chloride (p. 142), we are furnished with one of the cheapest means of preparing acids. Since hydrogen sulphate is **dibasic** (p. 245), it forms both acid and normal salts, such as $NaHSO_4$ and Na_2SO_4. The acid sulphates are called also bisulphates, because they contain twice as large a proportion of SO_4 to Na, and require twice as much sulphuric acid for their preparation as do the neutral sulphates.

4. Sulphuric acid combines vigorously with water to form at least one rather stable **hydrate,** H_2SO_4,H_2O (m.-p. 8°). On this account, sulphuric acid is able to take the elements of water from compounds containing hydrogen and oxygen, especially those containing these elements in the proportion 2H : O. Thus paper, which is largely cellulose $(C_6H_{10}O_5)_x$, wood which contains much cellulose, and sugar $C_{12}H_{22}O_{11}$ are charred by it, and carbon is set free:

$$C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O.$$

For the same reason, sulphuric acid is used in drying gases with which it does not interact.

5. On account of the large quantity of oxygen which hydrogen sulphate contains, and its instability when heated, it behaves as an **oxidizing agent.** This property has already been illustrated in connection with the action of the acid upon carbon, sulphur, and copper (p. 276), hydrogen iodide (p. 201), and hydrogen bromide (p. 196). The sulphuric acid is in consequence reduced to sulphur dioxide, and even to free sulphur or hydrogen sulphide. The metals, from the most active down to silver (p. 260), are capable of reducing it, the sulphates* being formed. The more active metals, like zinc, reduce it to hydrogen sulphide (p. 277), the less

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* Note that the sulphates, and *not* the oxides of the metals are produced. Oxides of metals could not be *formed in* concentrated sulphuric acid, because they interact with the latter much more vigorously than do the metals, to give the sulphates (*cf.* p. 146).

active, like copper, give sulphur dioxide (p. 276). Hydrogen is not liberated, because no hydrogen-ion is present in concentrated sulphuric acid. Gold and platinum alone do not interact with it. Free hydrogen itself is oxidized to water when passed into hydrogen sulphate at 160°: $SO_2(OH)_2 + H_2 \rightarrow SO_2 + 2H_2O$.

Concentrated sulphuric acid is **used** in almost all chemical industries: for example, to give sodium sulphate, as a stage in the Le Blanc process for the manufacture of soda; in the refining of petroleum; in the manufacture of fertilizers, such as superphosphate; in the preparation of nitroglycerine and gun-cotton, where it assists the action by removing water; and in the production of coal-tar dyes.

Chemical Properties of Aqueous Hydrogen Sulphate. — The solution of sulphuric acid H_2SO_4,Aq is a mixture, whose components are: undissociated molecules H_2SO_4, hydrogen-ion H^+, hydrosulphate-ion HSO_4^-, and sulphate-ion $SO_4^=$. The chemical properties shown by the solution are those of one or other of these components, according to circumstances.

Except in concentrated solutions (normal or stronger) the oxidizing effects of the undissociated, molecular substance are not encountered.

The presence of hydrogen-ion is shown by all its usual properties (p. 246).

Sulphate-ion $SO_4^=$, which is found also in solutions of all neutral and acid sulphates, unites with all positive ions. The product, when insoluble, appears as a precipitate. The introduction of barium ions, for example, by adding a solution of barium nitrate or chloride, is employed as a **test**:

$$Ba^{++} + SO_4^= \rightleftarrows BaSO_4\downarrow.$$

Since there are other barium salts which are insoluble in water (see Table of Solubilities), but no common ones which are not decomposed by acids, dilute nitric acid is first added to the solution supposed to contain the sulphate-ion. The other ions, even if present, then give no precipitate with barium-ion.

Dilute sulphuric acid is **used** for many purposes. Thus, it forms the liquid in the lead storage battery, and is employed for cleaning sheet iron before tinning and galvanizing.

Sulphates. — The **acid sulphates,** known also as **bisulphates,** (see p. 286), may be produced either by adding to dilute sulphuric acid half an equivalent of a base, and evaporating: $NaOH + H_2SO_4 \leftrightarrows H_2O + NaHSO_4$, or by actions in which another acid is displaced, as in making hydrogen chloride (p. 141). These salts are acid in reaction, as well as in name (*cf.* p. 269), because HSO_4^-, although a weak, is not a feeble acid. When heated, they yield pyrosulphates (p. 286).

The **normal** (or neutral) **sulphates** are obtained by complete neutralization and evaporation, or by the second of the above methods when a sufficient amount of the salt and a higher temperature are used:

$$NaCl + NaHSO_4 \rightleftarrows Na_2SO_4 + HCl\uparrow.$$

They may also be made by precipitation, by oxidation of a sulphide at a high temperature, $PbS + 2O_2 \rightarrow PbSO_4$, or by addition of sulphur trioxide to the oxide of a metal (p. 280).

Normal sulphates of the heavy metals decompose at a red heat, some giving off sulphur trioxide (p. 279), others sulphur dioxide and oxygen. The sulphates of the more active metals and of lead, however, are not affected by heating.

OTHER ACIDS OF SULPHUR

Sulphurous Acid H_2SO_3, Aq. — This term is applied to the solution of sulphur dioxide in water. A portion of the sulphur dioxide remains dissolved physically, while another portion is in combination with the water, forming sulphurous acid. This in turn is ionized, and chiefly, after the manner of the weaker dibasic acids, into two ions, H^+ and HSO_3^-. A little $SO_3^=$ is formed from the latter.

Properties of Sulphurous Acid. — The acid is so **unstable** that it cannot be obtained excepting in solution in water. Chemically it is a comparatively **weak acid.** As a **reducing agent,** it is slowly oxidized to sulphuric acid by free oxygen. Sugar and glycerine act as **negative contact agents** and make the oxidation much *slower.* It is oxidized more rapidly by oxidizing agents. Thus, when free halogens are added to the solution (*cf.* p. 161), sulphuric acid and the hydrogen halide are formed:

$$H_2SO_3 + HIO \rightleftarrows H_2SO_4 + HI.$$

Hydrogen peroxide, potassium permanganate, and other oxidizing agents convert the substance into sulphuric acid likewise.

Sulphurous acid has the power of **uniting directly** with many organic coloring matters and, since the products of this union are usually colorless, it is employed as a bleaching agent. It is especially useful with chemically reactive materials like silk, wool, and fragile structures like straw, which are likely to be destroyed if bleaching powder is used. The compounds thus formed are unstable, and lose the sulphurous acid again. Hence, wool yellows with age, and straw hats lose their whiteness. As a disinfectant it acts, perhaps, by addition likewise.

As a **dibasic acid,** sulphurous acid forms **normal salts** like Na_2SO_3, and **acid salts** like $NaHSO_3$.

Consecutive Reactions. — There are many chemical reactions that proceed in two stages, which can be carried out separately. This is the case with the two reactions used in the chamber process (p. 281). The actions are **consecutive,** because the second uses materials produced by the first. It may be noted that if the second action is as speedy as the first, or speedier, then no intermediate products will be detectable. This is the case with the chamber process reactions, when sufficient steam is introduced, for under these circumstances no solid nitrosylsulphuric acid is deposited. If the second reaction is slower than the first, then the products of the first reaction will accumulate, and become noticeable.

The conception of consecutive reactions enables us to understand and remember some facts. For example, it was mentioned that when dry sulphur is oxidized, we obtain sulphur dioxide, but when moist sulphur is oxidized, by the air or otherwise, the only product is sulphuric acid (p. 267). This change may be conceived of as proceeding in two stages:

$$\begin{aligned} S + O_2 + H_2O &\rightarrow H_2SO_3, \\ 2H_2SO_3 + O_2 &\rightarrow 2H_2SO_4, \end{aligned}$$

which would be consecutive reactions. Since oxidation of solid sulphur can proceed only on the surface, it is slow. Since the sulphurous acid is dissolved, and every molecule of it is accessible to the dissolved oxygen, or oxidizing agent, the second action should be speedier and consume the product of the first action as fast as it is formed. It is, therefore, quite natural that no sulphurous acid should be detectable when water is present.

Sulphites. — The **acid sulphites** of the alkali metals, $KHSO_3$ and $NaHSO_3$, when in solution, are acid in reaction, owing to the appreciable dissociation of the ion HSO_3^-. The sulphites are readily decomposed by acids to give free sulphurous acid, and the latter partly decomposes, yielding sulphur dioxide (p. 275).

Calcium bisulphite solution, $Ca(HSO_3)_2$, is used to dissolve the lignin out of wood, and leave the pure cellulose (paper pulp) employed in the manufacture of paper (*q.v.*).

When **heated,** sulphites undergo decomposition. The sulphates, being the most stable of *all* the salts of sulphur acids, are formed when the salts of *any* of those acids are decomposed by heating. The nature of the particular salt determines what other products shall appear. Thus, with sodium sulphite Na_2SO_3, one molecule of the sulphite furnishes three atoms of oxygen, sufficient to oxidize three other molecules, and leaves one molecule of sodium sulphide behind:

$$4Na_2SO_3 \rightarrow Na_2S + 3Na_2SO_4.$$

The sulphites are as readily **oxidized** as is the acid itself. They are slowly converted, both in solution and in the solid form, by the influence of the oxygen of the air, into sulphates.

Thiosulphuric Acid $H_2S_2O_3$. — This acid is not known in the free condition, but its salts are in common use in the laboratory and commercially. Sodium thiosulphate, for example, is prepared by boiling a solution of sodium sulphite with free sulphur. The action is something like the addition of oxygen to sulphurous acid:

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3 \quad \text{or} \quad SO_3^= + S \rightarrow S_2O_3^=.$$

Sodium thiosulphate ("hypo") is used in "fixing" photographs.

By the addition of acids to a solution of sodium thiosulphate, the thiosulphuric acid is set free, but the latter instantly decomposes, giving a precipitate of sulphur:

$$Na_2S_2O_3 + 2HCl \rightleftarrows H_2S_2O_3 + 2NaCl,$$
$$H_2S_2O_3 \leftrightarrows S\downarrow + H_2SO_3 \rightleftarrows H_2O + SO_2\uparrow .$$

Persulphuric Acid $H_2S_2O_8$. — This, like the other acids just mentioned, is unstable, and can be kept only in dilute solution. Its salts, however, are coming into use for commercial purposes and for "reducing" negatives in photography. The salts are prepared by electrolyzing sodium-hydrogen sulphate $NaHSO_4$ in concentrated solution (Hugh Marshall). The persulphuric acid, formed by the union of the negative ions in pairs as they are discharged on the anode,

$$2HSO_4^- + 2\oplus \rightarrow H_2S_2O_8,^*$$

undergoes double decomposition with the excess of sodium bisulphate, and the less soluble sodium persulphate crystallizes out. The other salts are made by double decomposition from this one.

Compounds of Sulphur and Chlorine. — When chlorine gas is passed over heated sulphur, it is absorbed and **sulphur monochloride,** a reddish-yellow liquid, boiling at 138°, is obtained. The molecular weight of this substance, as shown by the density of its vapor, indicates that it possesses the formula S_2Cl_2. When thrown into water, it is rapidly hydrolyzed, producing sulphur dioxide and sulphur: $2S_2Cl_2 + 2H_2O \rightarrow SO_2 + 4HCl + 3S$.

Sulphur itself dissolves very freely in the monochloride, and the solution is employed in vulcanizing rubber.

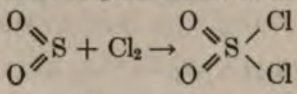
Sulphur dioxide and chlorine gases, when exposed to direct sunlight, unite to form a liquid known as **sulphuryl chloride** SO_2Cl_2. Camphor causes the union to take place much more rapidly, owing to some catalytic effect. The compound is a colorless liquid, boiling at 69°. With water it gives sulphuric acid and hydrogen chloride:

$$SO_2Cl_2 + 2H_2O \rightarrow SO_2(OH)_2 + 2HCl.$$

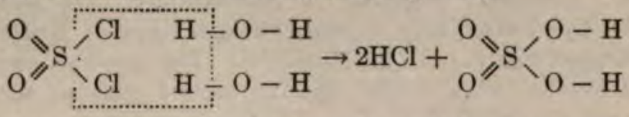
Graphic Formula of Sulphuric Acid. — The actions just mentioned give a clue to the constitution of sulphuric acid. Since

* See footnote, p. 276.

chlorine does not combine directly with oxygen, but does combine readily with sulphur, we may assume that, in the formation of sulphuryl chloride, $SO_2 + Cl_2 \rightarrow SO_2Cl_2$, the chlorine unites more intimately with the sulphur in the molecule SO_2:



The action of water upon the product is presumably similar to that of water on phosphorus tribromide (p. 197):



The last is called the **structural formula** of sulphuric acid. It is not thereby implied that the atoms in its molecules are attached precisely in this manner, however, but rather that the *chemical behavior* of the substance, as being partly an oxide and partly an hydroxide of sulphur, is symbolized in this fashion. Such **graphic formulæ** are of great value in expressing the chemical behavior of the complex compounds of carbon.

Exercises. — 1. What ground is there for assigning the formula SO_2 instead of S_2O_4 to sulphur dioxide (p. 277)?

2. Explain why nitric acid is completely displaced by the action of sulphuric acid on sodium nitrate (p. 282).

3. What are the relative volumes, (*a*) of sulphur dioxide and nitrogen (p. 150) resulting from the roasting of pyrite (p. 275), (*b*) of air and sulphur dioxide in making sulphuric acid, (*c*) of nitrogen (left) to sulphur dioxide (used) in making sulphuric acid, when pyrite is the source?

4. Make a list of, and classify, the various applications of sulphuric acid to the liberation of other acids.

5. Formulate the behavior of the hydrosulphate-ion (p. 287) when a solution of barium chloride is added to a rather concentrated solution of sulphuric acid.

6. Assign to the proper class of ionic actions (pp. 259, 270), (*a*) the action of iodine on sulphurous acid (p. 289), (*b*) of sulphur on sodium sulphite (p. 290), (*c*) the formation of persulphuric acid (p. 291).

CHAPTER XXII

SELENIUM AND TELLURIUM

THE CLASSIFICATION OF THE ELEMENTS

ALONG with sulphur, chemists group two other elements, selenium (Se, at. wt. 79.2) and tellurium (Te, at. wt. 127.5). If, while this and the next page are read, the nature of the chief compounds of sulphur is kept in mind, the analogy between the nature and chemical behavior of the three elements and their corresponding compounds will be obvious (see Chemical relations of the sulphur family, below).

Occurrence and Properties of Selenium Se. — Selenium (Gk., *the moon*) occurs free in some specimens of native sulphur, and in combination often takes the place of a small part of the sulphur in pyrite (FeS_2). It is found free in the dust-flues of the pyrite-burners of sulphuric acid works. The familiar forms are, the red precipitated variety, which is amorphous and soluble in carbon disulphide, and the lead-gray, semi-metallic variety, obtained by slow cooling of melted selenium, which is insoluble, and melts at 217°. In the latter form it has some capacity for conducting electricity, which is greatly increased by exposure to light in proportion to the intensity of the illumination. A photometer, using this property, has been devised by Joel Stebbins (1914), for measuring the relative intensity of the light of different stars. Selenium boils at 680°, and at high temperatures has a vapor density corresponding to the formula Se_2.

The element combines directly with many metals, burns in oxygen to form selenium dioxide, and unites vigorously with chlorine.

Compounds of Selenium. — Ferrous selenide, made by heating iron filings with selenium (*cf.* p. 13), when treated with concentrated hydrochloric acid gives hydrogen selenide:

$$FeSe + 2HCl \leftrightarrows H_2Se\uparrow + FeCl_2.$$

The compound is a poisonous gas, which possesses an odor recalling rotten horse-radish, and is soluble in water. The solution is faintly acid in reaction, and deposits selenium when exposed to the action of the air (*cf.* p. 270). Other selenides, which, with the exception of those of potassium and sodium, are insoluble in water, may be precipitated by leading the gas into solutions of soluble salts of appropriate metals (*cf.* p. 273).

The **dioxide** SeO_2 is a solid body formed by burning selenium. Selenious acid H_2SeO_3 may be made by dissolving the dioxide in hot water, or by oxidizing selenium with boiling nitric acid. Unlike sulphur (p. 267), the element gives little of the higher acid H_2SeO_4 by this treatment. The acid is reduced by sulphurous acid to selenium: $H_2SeO_3 + 2H_2SO_3 \rightarrow 2H_2SO_4 + H_2O + Se$.

No **trioxide** is known. **Selenic acid** H_2SeO_4, a white solid, is made in solution by oxidizing silver selenite with bromine-water (which contains hypobromous acid, *cf.* p. 161), and filtering:

$$\begin{array}{r}
Br_2 + H_2O \rightleftarrows HBr + HBrO. \\
Ag_2SeO_3 + HBrO \rightarrow Ag_2SeO_4 + HBr. \\
2HBr + Ag_2SeO_4 \rightarrow 2AgBr\downarrow + H_2SeO_4. \\
\hline
Br_2 + H_2O + Ag_2SeO_3 \rightarrow 2AgBr\downarrow + H_2SeO_4.
\end{array}$$

It is itself a powerful oxidizing agent and, even in dilute solution, liberates chlorine from hydrochloric acid: $H_2SeO_4 + 2HCl \rightarrow H_2SeO_3 + H_2O + Cl_2$. Sulphuric acid (*cf.* p. 286), on the other hand, is an oxidizing agent only in somewhat concentrated form, and even then it can oxidize hydrobromic acid (p. 196), but not hydrochloric acid.

Tellurium Te. — Tellurium (Lat., *the earth*) occurs in sylvanite in combination with gold and silver. It is a white, metallic, crystalline substance, melting at 452° (b.-p. 1400°). The free element unites with metals directly, and burns in air to form the dioxide.

The compounds of tellurium are similar in composition and mode of preparation to those of selenium. Some differences in chemical behavior are significant, however. Thus, **tellurious acid** H_2TeO_3 is a very feeble acid and is also somewhat basic, a sulphate ($2TeO_2$, SO_3) and a nitrate ($Te_2O_3(OH)NO_3$) being known. In this respect it differs markedly from sulphurous acid. **Telluric acid** does not affect indicators, and is therefore actually more feebly acidic than is hydrogen sulphide. **Tellurium tetrachloride** $TeCl_4$, although hydrolyzed by water, exists in solution with excess of hydrogen chloride: $TeCl_4 + 3H_2O \rightleftarrows H_2TeO_3 + 4HCl$, showing the tellurious acid to be basic in properties and the element tellurium to be, to a certain degree, a metallic element.

The Chemical Relations of the Sulphur Family. — It will be seen that sulphur, selenium, and tellurium are bivalent elements when combined with hydrogen or metals. In combination with oxygen they form unsaturated compounds of the form $X^{IV}O_2$, while their highest valence is found in SO_3, TeO_3, and H_2SeO_4, where they must be sexivalent. The general behavior of corresponding compounds is very similar. At the same time, there is in all cases a progressive change as we proceed from sulphur through selenium to tellurium. The elementary substances themselves, for example, become more like metals, physically, and they show higher and higher melting-points. The affinity for hydrogen decreases, as is shown by the increasing ease with which the compounds H_2X are oxidized in air. The affinity for oxygen likewise decreases, for the elements become increasingly difficult to raise to the highest state of oxidation. On the other hand, the tendency to form higher chlorides becomes greater. We note also that the compounds H_2XO_4 become less and less active as acids, and that a basic tendency begins to assert itself.

THE PERIODIC SYSTEM

Classification, or the arrangement of facts on the basis of likeness, is part of the method of science. It is needed to make possible the systematic description of the ascertained facts, which is a great aid to the memory, and to furnish a guide in investigation, by suggesting relations and so pointing out directions in which new facts of interest may be found. Thus, as an aid to memory, we have treated the halogens as one family and S, Se, and Te as another. In each case, we have presented the properties common to all members of the group, and have then pointed out the differences. Again, in investigation, as soon as we have discovered that sulphur and selenium are allied elements, we realize the direction in which fruitful results may be expected, and we proceed to make the corresponding compounds and to note the resemblances and differences in the conditions for preparation and in the properties of the compounds obtained.

Metallic and Non-Metallic Elements. — Thus far we have found the division into metallic and non-metallic elements very serviceable for classification in terms of chemical relations (p. 163). This distinction we shall continue to employ. **The metallic, or positive elements** (p. 94), (1) form positive radicals and ions containing no other element (*cf.* p. 247). Thus the metals give sulphates, nitrates, carbonates, and other salts, which furnish a metallic ion, such as Na^+ or K^+, together with the ions $SO_4^=$, NO_3^-, and $CO_3^=$. (2) Their hydroxides, KOH, $Ca(OH)_2$, etc., give the same metallic ion, and the rest of the molecule forms hydroxide-ion. That is to say, their hydroxides are bases and their oxides are basic. The metallic elements often enter, but only *with other elements*, into the composition of a negative ion, as is the case with manganese in $K.MnO_4$, with chromium in $K_2.Cr_2O_7$, and with silver in $K.Ag(CN)_2$.

The non-metallic or negative elements (1) are found chiefly in negative radicals and ions. They form no nitrates, sulphates, carbonates, etc., for they could not do so without themselves alone constituting the positive ion. We have no such salts of sulphur, carbon, or phosphorus, for example. (2) Their hydroxides, although their formulæ may be *written* ClO_2OH, $P(OH)_3$, $SO_2(OH)_2$, furnish no hydroxyl ions, as this would involve the same consequence. These hydroxides are divided by dissociation, in fact, so that the non-metal forms part of a compound negative radical, and the other ion is hydrogen-ion, $ClO_3.H$, $PO_3H.H_2$, $SO_4.H_2$. Their oxides are acidic. (3) Their halogen compounds, like PBr_3 (p. 197) and S_2Cl_2 (p. 291), are completely hydrolyzed by water, and the actions are not, in general, reversible. The halides of the *typical* metals are not hydrolyzed (see Chap. XXXIII), and with those that are not typical, the action is reversible.

The distinction is not perfectly sharp, however. Thus, zinc gives both salts like the sulphate, $Zn.SO_4$, and chloride, $Zn.Cl_2$, and compounds like sodium zincate (p. 56), $ZnO_2.Na_2$.

Classification by Atomic Weights. — Newlands (1863–4) discovered a surprising regularity that became apparent when the elements were placed in the order of ascending atomic weight. Omitting hydrogen (at. wt. 1) the first seven were: lithium (7), glucinum (9), boron (11), carbon (12), nitrogen (14), oxygen (16), fluorine (19). These are all of totally different classes, and include first a metal forming a strongly basic hydroxide, then a metallic element of the less active sort, then five non-metals of increasingly negative character, the last being the most active non-metal known. The next element after fluorine (19) was sodium (23), which brings us back sharply to the elements that form strongly basic hydroxides. Omitting none, the next seven elements were sodium (23), magnesium (24.4), aluminium (27), silicon (28.4), phosphorus (31), sulphur (32), chlorine (35.5). In this series there are three metals of diminishing positiveness, followed by four non-metals of increasing negative activity, the last being a halogen very like fluorine. On account of the fact that each element resembles most closely the eighth element beyond or before it in the list, the relation was called the **law of octaves.** After chlorine the octaves become less easy to trace.

That this periodicity in chemical nature is more than a coincidence is shown by the fact that the valence and even the physical properties, such as the specific gravity, show a similar fluctuation in each series. In the first two series the compounds with other elements are of the types:

$$\mathrm{LiCl},\ \mathrm{GlCl_2},\ \mathrm{BCl_3},\ \mathrm{CCl_4},\ \left\{\begin{array}{l}\mathrm{N_2O_5}.\\ \mathrm{NH_3},\ \mathrm{OH_2},\ \mathrm{FH}.\end{array}\right.$$

$$\mathrm{NaCl},\ \mathrm{MgCl_2},\ \mathrm{AlCl_3},\ \mathrm{SiCl_4},\ \left\{\begin{array}{l}\mathrm{P_2O_5},\ \mathrm{SO_3},\ \mathrm{Cl_2O_7}.\\ \mathrm{PH_3},\ \mathrm{SH_2},\ \mathrm{ClH}.\end{array}\right.$$

Thus the valence towards chlorine or hydrogen ascends to four and then reverts to one in each octave. The highest valence, shown in oxygen compounds, ascends from lithium to nitrogen with values one to five, and then fails because compounds are lacking. In the second octave, however, it goes up continuously from one to seven.

Again, the specific gravities of the elements in the second series, using the data for red phosphorus and liquid chlorine, are:

Na 0.97, Mg 1.75, Al 2.67, Si 2.49, P 2.14, S 2.06, Cl 1.33.

Mendelejeff's Scheme. — In 1869 Mendelejeff published an important contribution towards adjusting the difficulty which the elements following chlorine presented, and developed the whole conception so completely that the resulting system of classification has been connected with his name ever since. Almost simultaneously Lothar Meyer made similar suggestions, but did not urge them with the same conviction or elaborate them so fully. The table on the following page, in which the atomic weights are expressed in round numbers, is a modification of one of Mendelejeff's.

The chief change from the arrangement in simple octaves is that the third series, beginning with potassium, is made to furnish material for two octaves, potassium to manganese and copper to bromine, and is called a **long series.** The valences fall in with this plan fairly well. Copper, while usually bivalent, forms also a series of compounds in which it is univalent. Iron, cobalt, and nickel cannot be accommodated in either octave, as their valences are always two or three. At the time Mendelejeff made the table, three places in the third long series had to be left blank, as a trivalent element [Sc] was lacking in the first octave of the series, and a trivalent [Ga] and a quadrivalent one [Ge] in the second. These places have since been filled, as we shall presently see. The first two (the *short*) series have been split in the table, as lithium and sodium closely resemble potassium, while the remaining members of these series fall more naturally over the corresponding elements of the second octave of the third series.

The fourth series (long) is nearly complete. It begins with an active alkali metal, rubidium, and ends with iodine, a halogen. The rule of valence is strictly preserved throughout the series, and in general the elements fall below those which they most closely resemble.

The fifth, sixth, and seventh (long) series are incomplete, but the order of the atomic weights and the valence enable us satisfactorily to place all but about ten rare elements. The chemical relations to elements of the fourth series justify the position assigned to each. Cæsium, for example, is the most active of the alkali metals; barium has always been classed with strontium, and bismuth with antimony.

In two cases a slight displacement of the order according to atomic weights is necessary. Cobalt is put before nickel because it

ONE OF MENDELEJEFF'S TABLES, MODIFIED

Li 7	....	....	....	....	....	....	....	....	....	....	Gl 9	B 11	C 12	N 14	O 16	F 19
Na 23	....	....	....	....	....	....	....	....	....	....	Mg 24.3	Al 27	Si 28.3	P 31	S 32	Cl 35.5
K 39	Ca 40	[Sc] 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 59	Ni 58.7	Cu 63.6	Zn 65.4	[Ga] 70	[Ge] 72.5	As 75	Se 79.2	Br 80
Rb 85.5	Sr 87.6	Y 89	Zr 90.6	Cb 93.5	Mo 96	....	Ru 101.7	Rh 103	Pd 106.7	Ag 108	Cd 112.4	In 115	Sn 119	Sb 120	Te 127.5	I 126.9
Cs 133	Ba 137.4	La 139	Ce 140	Nd 144.3	....	....	....	....	....	....	....	....	....	....	....	....
....	....	Yb 173.5	....	Ta 181.5	W 184	....	Os 191	Ir 193	Pt 195	Au 197	Hg 200.6	Tl 204	Pb 207	Bi 208	....	....
....	Ra 226	....	Th 232.4	....	U 238.2	....	....	....	....	....	....	....	....	....	....	....

resembles iron more closely. Tellurium and iodine are placed in that order to bring them into the sulphur and halogen groups respectively. Their valence and other chemical relations both require this. The general agreement, however, is very remarkable.

General Relations in the System. — In every octave the **valence** towards oxygen ascends from one to seven, while that towards hydrogen, in the cases of the last four elements (when they combine with hydrogen at all), descends from four to one. The **physical properties** fluctuate within the limits of each series in a similar way. The values of each physical constant for corresponding members of the **successive** series do not exactly coincide, however. A progressive change, as we descend each vertical column, is the rule. Thus the specific gravities (water = 1) of the alkali metals rise from lithium (0.53) to cæsium (1.87). In the same group the melting-points descend from lithium (186°) to cæsium (26.5°).

As yet no exact mathematical (quantitative) relation between the values for any property and the values of the atomic weights has been discovered; only a general (qualitative) relationship can be traced. Anticipating the discovery of some more exact mode of stating the relationship in each case, and remembering that similar values of each property recur *periodically*, usually at intervals corresponding to the length of an octave or series, the principle which is assumed to underlie the whole, the **periodic law,** is stated thus: **All the properties of the elements are periodic functions of their atomic weights.**

That the **chemical relations** of the elements vary just as do the physical properties of the simple substances is easily shown. Thus, each series begins with an active metallic (positive) element, and ends with an active non-metallic (negative) element, the intervening elements showing a more or less continuous variation between these limits. Again, the elements at the top are the least metallic of their respective columns. As we descend, the members of each group are more markedly metallic (in the first columns), or, what is the same thing, less markedly non-metallic (in the later columns; *cf.* p. 296).

In the first series boron is the first non-metal we encounter. In the second series silicon is the first such element. In the third there is more difficulty in deciding. Titanium, vanadium, and germanium are usually, though with questionable propriety, classed as metallic elements.* Selenium is undoubtedly non-metallic. Arsenic is, on the whole, non-metallic. In the fourth series tellurium is commonly considered to be the first non-metallic element. Thus a zigzag line, shown in the table, separates all the non-metallic elements from the rest of the elements, and confines them in the right-hand upper corner.

A more compact form of the table is printed at the end of this book, opposite the rear cover. The only difference between this and the other is that the two octaves of each long series have been placed in the same set of seven main columns. The iron, palladium, and platinum groups occupy a column on the right of the main columns, and are often called collectively the eighth group. The newly discovered elements, found chiefly in the air, have been placed at the left-hand side. Since they do not enter into combination at all, their valence may appropriately be given as zero. With the exception of argon, the values of their atomic weights agree well with this assignment. Hydrogen is the only common element whose place is still in debate. The valence is shown by the general formulæ at the head of each column.

Applications of the Periodic System. — The system has found application chiefly in four ways:

1. In the **prediction of new elements.** Mendelejeff (1871) drew attention to the blank then existing between calcium (40) and titanium (48). He predicted that an element to fit this place would have an atomic weight 44 and would be trivalent. From the nature of the surrounding elements, he very cleverly deduced many of the physical and chemical properties of the unknown element and of its compounds. In 1879 Nilson discovered scandium (44), and its behavior corresponded closely with that predicted. Mendelejeff described accurately two other elements, likewise unknown at the time. In 1875 Lecoque de Boisbaudran found gallium, and in 1888 Winkler discovered germanium, and these blanks were filled.

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* In discussing chemical relations, the term **metallic element** is preferable to **metal.** The free element (*e.g.*, arsenic) may have the luster of a metal, and yet the element, in combination, may be non-metallic or negative.

2. By enabling us to decide on the **correct values for the atomic weights** of some elements, when the equivalent weights have been measured, but no volatile compound is known (*cf.* pp. 104 and 118). Thus, the equivalent weight of indium was 38 and, as the element was supposed to be bivalent, it received the atomic weight 76. It was quite out of place near arsenic (75), however, being decidedly a metallic element. As a trivalent element with the atomic weight 115, it fell between cadmium and tin. Later work fully justified the change. Quite recently, radium has been discovered, and found to have the equivalent weight 113 and to resemble barium. If, like barium, it is bivalent, it occupies a place under this element, in the last series.

3. By **suggesting problems for investigation.** The periodic system has been of constant service in the course of inorganic research, and has often furnished the original stimulus to such work as well. For example, the atomic weight of tellurium bore the value 128 when the table was first constructed, and it was confidently expected that reëxamination would bring this value below that of iodine (then 127, now 126.92). Several most careful studies of the subject have been made by different methods. It seems probable that the real value of the atomic weight is not far from Te = 127.5, and therefore more than half a unit greater than that of iodine. Since, however, mathematical correspondence is found nowhere in the system, the existence of marked inconsistencies like this need not shake our confidence in its value when it is used with due consideration of the degree of correspondence to be expected.

In the same way, incorrect values of many physical properties have been detected, and have been rectified by more careful work.

4. By furnishing a comprehensive **classification of the elements,** arranging them so as to exhibit the relationships among the physical and chemical properties of the elements themselves and of their compounds. Constant use will be made of this property of the table in the succeeding chapters. Having disposed of the halogen and sulphur families (excepting the oxygen compounds of the former), situated, respectively, in the seventh and sixth columns of the table (at the end of this book), we shall presently take up nitrogen and phosphorus from the right side of the fifth column. Then from the fourth column, we shall select carbon and silicon,

and from the third boron, leaving the other, more decidedly metallic elements for later treatment.

Moseley's Atomic Numbers. — We have seen that simple, mathematical relations between the atomic weights and the physical or chemical properties of an element do not exist. In several instances, the atomic weights are not even in the same order as are the values of the properties. We have now obtained from another direction numbers which seem to be more fundamental even than atomic weights.

Visible light, X-rays, and wireless electric waves are all vibrations of the same nature in the ether. They differ only in wave-length, the order of the wave-lengths being 10^{-5} cm., 10^{-8} cm., and 10^{6} cm. (10 kilometers), respectively. Now, just as the spectrum of visible light is obtained by using a grating, on which the rulings are separated by distances of the order of the wave-length of such light, so ordinary crystals give spectra of X-rays, because they are composed of particles arranged in rows about one thousand times closer and so form a suitable grating for X-rays. This fact was first discovered by Dr. Laue of the University of Zurich (1912). The X-rays are produced in an evacuated tube by cathode rays, which are streams of electrons emanating from the cathode (C, Fig. 88), when they strike the anticathode (A).

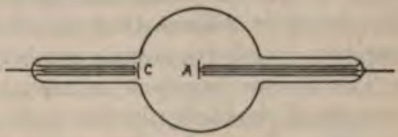


Fig. 88.

With different elements on the anti-cathode, X-rays of slightly different wave-lengths, and therefore giving different X-ray spectra, are produced. By using different elements, Moseley (1914) has found that the higher the atomic weight the shorter the wave-length of the characteristic X-rays. When the elements are arranged in the order of these wave-lengths, whole numbers can be assigned to each which are inversely proportional to the square roots of the wave-lengths of corresponding lines in their X-ray spectra. These **atomic numbers** have been determined for most of the elements, the atomic weights of which lie between those of aluminium and gold. In the following table, the atomic numbers for these elements are given and numbers for the twelve elements preceding Al have been inserted also.

ATOMIC NUMBERS (Moseley)

H 1	He 2	Li 3	Gl 4	B 5	C 6	N 7	O 8	F 9	.....	.....	.....
......	Ne 10	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	.....	.....	.....
......	A 18	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28
......	.....	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	.....	.....	.....
......	Kr 36	Rb 37	Sr 38	Y 39	Zr 40	Cb 41	Mo 42	— 43	Ru 44	Rh 45	Pd 46
......	.....	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	.....	.....	.....
......	Xe 54	Cs 55	Ba 56	La 57	Ce 58	Ta 73*	W 74	— 75	Os 76	Ir 77	Pt 78
......	.....	Au 79	.....	.....	.....	.....	.....	.....	.....	.....	.....

* The atomic numbers 59–72 are those of the metals of the rare earths: Pr 59, Nd 60, –61, Sa 62, Eu 63, Gd 64, Tb 65, Dy 66, Ho 67, Er 68, Tm 69, Yb 70, Lu 71, –72.

It will be seen that there is a whole number available for every known element, up to and including gold, and not omitting the rare elements which have no satisfactory place in the periodic system. There are two blank numbers in the table, which correspond to two spaces below Mn in the periodic system, and two more amongst the rare elements, indicating only four elements with atomic weights less than that of gold yet to be discovered. The atomic numbers of argon and potassium place them in the chemically correct order, while the atomic weights do not. The same is true of cobalt and nickel and of tellurium and iodine. Finally, it is evident that the atomic weight of each element is, roughly, double its atomic number.

The atomic numbers represent the number of unit positive charges of electricity in the nucleus of the atom of each element (p. 235). Rutherford has shown that the nucleus contains almost the whole mass of the atom, although one or more electrons (negative) are present also. Thus, the positive nucleus of the hydrogen atom is 1800 times heavier than one electron. The nucleus, however, is very minute, having a diameter only about one-eighteen hundredth of that of an electron.

The atomic numbers apparently determine all the properties of each element, and are more fundamental than the atomic weights. The latter are secondary properties, in most cases modified by other factors, and in a few cases actually thrown out of order by such factors.

Crystal Structure. — In this connection it may be mentioned that by using crystals of different substances as X-ray gratings,

W. L. Bragg (1914) has been able to measure the distances between the rows of particles in crystals. He also finds that the particles, the regular arrangement of which gives the structure (p. 82) of the crystal (*e.g.*, a cube of common salt), are not the molecules of the compound, much less aggregates of such molecules, but the atoms of the constituent elements. It would thus appear that the physical forces (if we may call them physical) which hold the crystalline solid together have completely crushed the chemical, molecular structure out of existence, and have arranged the constituent atoms, as the units of the structure, in a crystallographic pattern. Of course, when the crystal-form is destroyed, by melting, solution, or vaporization, the neighboring atoms remain united in groups, constituting the chemical molecules of the substance.

Exercises. — 1. Can you explain the presence of *free* selenium in the flues of pyrite burners (p. 294)?

2. How should you attempt to obtain H_2Te, and what physical and chemical properties should you expect it to possess?

3. Make a list of bivalent elements and criticize this method of grouping as a means of chemical classification.

4. Write down the symbols of the elements in the fourth series (that beginning with rubidium, and ending with iodine) on p. 299. Record the valence of each element toward oxygen, using for reference the chapters in which the oxygen compounds are described.

CHAPTER XXIII

OXIDES AND OXYGEN ACIDS OF THE HALOGENS
OXIDATION AND REDUCTION

THE chief subjects of practical importance touched upon in the first part of this chapter are connected with bleaching powder $CaCl(OCl)$, and potassium chlorate $KClO_3$ and perchlorate $KClO_4$. Hence our attention will be largely directed to the modes of making these substances and to their relations to one another. Incidentally, we shall encounter many actions of a complex and, to us, more or less novel kind.

Compounds of Chlorine Containing Oxygen. — The following are the names and formulæ of the substances:

$HClO$ Hypochlorous acid,	Cl_2O Hypochlorous anhydride,
$[HClO_2]$ Chlorous acid,	. . . .
. . . .	ClO_2 Chlorine dioxide,
$HClO_3$ Chloric acid,	. . . .
$HClO_4$ Perchloric acid,	Cl_2O_7 Perchloric anhydride.

There are also salts of these acids, like the three substances mentioned in the first paragraph. Chlorous acid is itself unknown, but potassium chlorite $KClO_2$ and some other derivatives have been made.

The two anhydrides (p. 94), when brought into contact with water, combine with it to form the acids opposite which they stand in the table. Chlorine dioxide (*q.v.*), however, is not related to any one acid in this way.

All these compounds differ from most that we have hitherto discussed, inasmuch as not one of them can be made by direct union of the simple substances.

Nomenclature of the Acids and their Salts. — The acids and salts are named on a plan similar to that used in the case of the sulphur acids:

KClO	Potassium *hypo*chlor*ite*,	HClO	*Hypo*chlor*ous* acid,
$KClO_2$	Potassium chlor*ite*,	$HClO_2$	Chlor*ous* acid,
$KClO_3$	Potassium chlor*ate*,	$HClO_3$	Chlor*ic* acid,
$KClO_4$	Potassium *per*chlor*ate*.	$HClO_4$	*Per*chlor*ic* acid.

It should be noted, however, that the use of *ic* and *ous* for more and less oxygen, respectively, and of *hypo* for still less and of *per* for still more oxygen are simply relative terms *within a single group*. Thus, sulphur*ic* acid H_2SO_4 has a composition entirely different from chlor*ic* acid, and both of these differ in composition from phosphor*ic* acid H_3PO_4. The names and formulæ of each group must be learned, separately.

Chlorine Monoxide or Hypochlorous Anhydride Cl_2O. — A solution of pure hypochlorous acid is most easily prepared by dissolving the anhydride in water. This oxide is obtained by passing chlorine gas over warmed mercuric oxide* HgO (Fig. 66, p. 156). Each of the constituents of the oxide combines with chlorine:

$$HgO + 2Cl_2 \rightarrow HgCl_2 + Cl_2O.$$

The mercuric chloride then unites with another formula-weight of the mercuric oxide to form a solid basic mercuric chloride HgO, $HgCl_2$, which remains in the tube. The chlorine monoxide is a brownish-yellow, heavy, easily liquefied gas (b.-p. 5°). When slightly warmed it decomposes into its constituents with explosion. The gas dissolves in water very easily (200 : 1, by vol.). The yellow solution of hypochlorous acid which results:

$$Cl_2O + H_2O \leftrightarrows 2HOCl,$$

has a strong odor of chlorine monoxide, because the combination is reversible. There are other ways of preparing a *dilute* solution of the acid (see below).

Properties of Hypochlorous Acid. — Hypochlorous acid is unstable, and cannot be made, excepting in solution, or kept, excepting in dilute solution. This is in consequence of its tendency to decompose in three different ways, one of which, the liberation of the anhydride, has just been mentioned.

---

* The crystalline, red oxide is not sufficiently active. The oxide must be precipitated from sodium hydroxide and mercuric nitrate solutions, it must be washed thoroughly on a filter, and be dried at 300–400° before use.

1. Hypochlorous acid is a little-ionized, weak *acid.*

$$HOCl \rightleftarrows H^+ + ClO^-.$$

It neutralizes active bases, its ionization equilibrium being displaced forwards as the hydrogen-ion H^+ is removed to form water:

$$NaOH + HOCl \rightleftarrows NaOCl + H_2O.$$

2. The solution, if strong, gives off chlorine monoxide Cl_2O, the union with water being reversible.

3. If the solution is concentrated, much of the hypochlorous acid changes gradually into chloric acid and hydrogen chloride. This is a self-oxidation. It occurs even in the dark:

$$3HOCl \rightarrow HClO_3 + 2HCl.$$

4. When the solution is exposed to sunlight, oxygen is evolved rapidly.

$$2HOCl \rightarrow 2HCl + O_2.$$

This decomposition always takes place in sunlight, whether the acid is present alone in the water, or along with other substances. We have already noted this fact in discussing chlorine-water (p. 162), which contains this acid.

5. In consequence of the ease with which it gives up oxygen, hypochlorous acid is a strong oxidizing agent. In this direction it has several important commercial applications (see below).

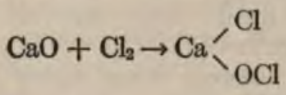
Commercial Preparation of Hypochlorites. — For commercial purposes, pure hypochlorites are not, as a rule, required. Hence, **sodium** or **potassium hypochlorite** is prepared by the action of sodium or potassium hydroxide on chlorine-water. The latter contains both hydrochloric and hypochlorous acids, and so a solution containing a mixture of sodium or potassium chloride and hypochlorite is obtained:

$$Cl_2 + H_2O \rightleftarrows HCl + HOCl. \quad (1)$$
$$HCl + KOH \rightleftarrows KCl + H_2O. \quad (2)$$
$$HOCl + KOH \rightleftarrows KOCl + H_2O. \quad (3)$$

Although action (1) is only partial, being strongly reversible, the neutralization of the two acids in actions (2) and (3) displaces the first equilibrium, and all three actions proceed to completion. Action (1), followed by (2) or (3), is a pair of consecutive actions (p. 289), of which the second (the neutralization) is the speedier of the two. Both pairs of consecutive actions (1) + (2) and (1) + (3), can be combined in one equation. Thus, omitting the water, which appears both among products and initial substances and in any case is present in large excess as a solvent, and omitting also the two acids, which are used up as quickly as they are produced by equation (1) and are not amongst the actual products, we get, by addition of the three equations (*cf.* p. 195), the final equation:

$$Cl_2 + 2KOH \rightarrow KCl + KOCl + H_2O.$$

As lime is a less expensive alkali than is potassium or sodium hydroxide, it is largely used. The chlorine is led into chambers containing quicklime CaO spread on trays:



$$CaO + Cl_2 \rightarrow Ca\begin{matrix} \diagup Cl \\ \diagdown OCl \end{matrix}$$

The product is not a mixture, but a mixed salt (p. 245), known as **bleaching powder** or "chloride of lime." The fact that this is a mixed salt does not interfere with its use as a commercial source of hypochlorous acid. It is only moderately soluble in water.

Hypochlorous Acid from Bleaching Powder. — 1. When bleaching powder is dissolved in water, being a salt, it is very extensively ionized (see formulation). If now an *active* acid, that is, one giving a large concentration of hydrogen-ion, is added, the values of the products of the concentrations $[H^+] \times [Cl^-]$ and $[H^+] \times [OCl^-]$, on which depend the extent to which molecules of HCl and HOCl will be formed (p. 238), are large. HClO, being little ionized, is formed extensively: HCl, being highly ionized is formed in much smaller amount. Both, however, interact to produce chlorine and water, and this displaces the other equilibria. Hence an active acid decomposes the salt almost completely. An

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

It also oxidizes bromine and iodine, in water, although these elements are not affected by free oxygen, giving bromic and iodic acids, respectively:

$$5HClO + I_2 + H_2O \rightarrow 5HCl + 2HIO_3.$$

The solution also oxidizes organic colored substances (p. 221), producing colorless, or less strongly colored ones. Thus, it oxidizes indigo (deep blue) quickly to isatin, a yellow substance relatively pale in color:

$$C_{16}H_{10}N_2O_2 + 2HOCl \rightarrow 2C_8H_5NO_2 + 2HCl.$$

In ways just as definite as this, hypochlorous acid will change the composition of other colored substances, although, since we do not know the formulæ of all these substances, we cannot always write equations for the actions.

Hypochlorous Acid as a Bleaching Agent. — It is on account of its oxidizing power that hypochlorous acid is used commercially in **bleaching.** It is not applied to paints, which are chiefly mineral substances, but to complex compounds of carbon, such as constitute the coloring matters of plants and of those artificial dyes which are now manufactured in great variety.

Cotton and linen, in their original states, are not pure white. Bleaching is, therefore, an extensive and most important industry. The yarn or cloth must first be freed from cotton-wax and tannin, since the former would protect it from the action of the bleaching agent, and both would make the subsequent dyeing uneven. The material is, therefore, first boiled with very dilute sodium hydroxide solution, and washed with water. The goods are then saturated with bleaching powder solution, and piled loosely until the coloring matter has been oxidized. They are finally washed with extreme thoroughness.

As a rule, an active acid is not added. The bleaching is produced by the hypochlorous acid liberated by the action of the carbon dioxide from the air. The carbon dioxide dissolves in the water of the solution on the goods, and forms carbonic acid: $CO_2 + H_2O \rightleftarrows H_2CO_3$ (see p. 310, par. 2). The subsequent washing removes all traces of the bleaching powder, of the lime which the powder often contains, and of the hypochlorous acid, which [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] and [illegible] bleaching agent. [illegible] [illegible] [illegible] [illegible] [illegible] with[illegible] [illegible] [illegible] washing [illegible] [illegible] [illegible] [illegible] damage [illegible] [illegible] [illegible].

Cotton and linen are composed of cellulose [illegible], a rather inert substance, and are [illegible] a very strong action [illegible] by dilute hypochlorous acid. Hence [illegible] [illegible] [illegible] and [illegible] bleaching [illegible] [illegible] [illegible]. Wool, silk, and feathers, however, are composed largely of complicated proteins containing nitrogen [illegible] [illegible] [illegible] [illegible] [illegible] the above three elements. Their [illegible] [illegible] [illegible] [illegible] with hypochlorous acid as [illegible] [illegible] coloring substances. Hence [illegible] [illegible] itself would be attacked by this agent. Sulphur dioxide or sulphurous acid (p. [illegible]) is used for bleaching these materials.

Bleaching Powder in Sanitation. — A disinfectant is a substance which destroys bacteria and other minute organisms. Bleaching powder has a distinct odor of chlorine [illegible] and [illegible]. This is due to the action of atmospheric carbonic acid [illegible] hypochlorous acid (p. [illegible]). The dry powder [illegible] will disinfect the air and surrounding objects. It must be used with discretion, however, as the gas is very irritating.

In recently introduced [illegible] (p. [illegible]) in the purification of city waters the organisms which give rise to typhoid fever are destroyed by adding a small proportion of bleaching powder solution, about 30 lbs. per million gallons of water. The salt is hydrolyzed (p. [illegible]), giving a trace calcium chloride and free hypochlorous acid. The latter kills the organisms, and is itself decomposed in the process, so that nothing offensive remains in the water. There is only a minute increase in the proportion of salts of calcium (hardness).

Recently, chlorine-water, made by use of cylinders of liquid chlorine (p. [illegible]), has in many cases taken the place of bleaching powder solution for this purpose.

Chlorine not a Bleaching Agent. — Chlorine itself is often, erroneously, described as a bleaching agent. If a dry, colored cloth be hung for a week in chlorine gas, dried by a little sulphuric acid in the bottom of the bottle (Fig. 89), little or no change in the color will occur. But a *wet* rag is bleached as soon as the chlorine has time to dissolve in the water and give the necessary hypochlorous acid. Flowers are bleached by dry chlorine gas, because by their nature they contain the indispensable water.

Chemical Properties of Hypochlorites. — When hypochlorites are heated they change into chlorates (see below). They may also give off oxygen, $2CaCl(OCl) \rightarrow 2CaCl_2 + O_2$. Although this decomposition is slow in cold solutions of hypochlorites, or when they are preserved in the dry form, it may be hastened by means of catalytic agents. The addition of a little cobalt hydroxide (*q.v.*) to a paste of bleaching powder and water causes rapid evolution of oxygen.

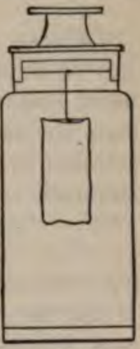


FIG. 89.

Chlorates. — Like hypochlorous acid itself, the hypochlorites turn into chlorates. Thus, when chlorine is passed into a *warm*, concentrated solution of potassium hydroxide, and particularly when an excess of chlorine is used, the potassium hypochlorite changes into **potassium chlorate** $KClO_3$ as fast as it is formed. Since this action (equation 2) requires 3KClO, the equation formerly given (p. 309) must be tripled:

$$\begin{array}{ll} & 3Cl_2 + 6KOH \rightarrow 3KCl + 3KClO + 3H_2O. \qquad (1) \\ & \underline{\qquad\quad 3KClO \rightarrow 2KCl + KClO_3. \qquad\quad} \qquad (2) \\ \text{Adding:} & 3Cl_2 + 6KOH \rightarrow KClO_3 + 5KCl + 3H_2O. \end{array}$$

When the solution is cooled, the less soluble chlorate crystallizes.

This action involves converting five-sixths of the valuable potassium hydroxide into the relatively less valuable potassium chloride. Hence, in practice, the makers carry out the corresponding action with calcium hydroxide. They then add potassium chloride to the resulting solution, containing calcium chloride (very soluble) and **calcium chlorate** $Ca(ClO_3)_2$. The potassium chlorate, formed by double decomposition, crystallizes when the solution is cooled.

All chlorates are at least moderately soluble in water (see Table inside of front cover). Potassium chlorate is **used** in making fireworks, explosives, and matches. An intimate mixture with sugar $C_{12}H_{22}O_{11}$ burns with semi-explosive violence, the oxygen of the salt combining with the carbon and hydrogen of the sugar to form carbon dioxide and water.

Chloric Acid $HClO_3$. — Since none of the acids of this series can be obtained by direct union of their elements (p. 306), it is usual first to prepare the salts, and to make the acids from the salts by double decomposition. This acid may be obtained, in solution in water, by adding the calculated amount of diluted sulphuric acid to a solution of barium chlorate:

$$Ba(ClO_3)_2 + H_2SO_4 \leftrightarrows BaSO_4\downarrow + 2HClO_3.$$

The barium sulphate, being insoluble, is removed by filtration. It will be noted that double decomposition involving **precipitation may** thus **be used for obtaining a soluble product,** as well as an insoluble one (*cf.* selenic acid, p. 294).

The solution may be concentrated (to about 40 per cent) by evaporation, but must not be heated above 40°, as the acid decomposes near this temperature. The resulting thick, colorless liquid has powerful oxidizing qualities, setting fire to paper (made of cellulose $(C_6H_{10}O_5)_x$) which has been dipped into it. It converts iodine into iodic acid, $2HClO_3 + I_2 \rightarrow 2HIO_3 + Cl_2$. When not in solution, or when warmed in solution beyond 40°, the acid decomposes, giving **chlorine dioxide** and **perchloric acid:**

$$3HClO_3 \rightarrow H_2O + 2ClO_2 + HClO_4.$$

Chlorine Dioxide: Chlorous Acid. — **Chlorine dioxide** ClO_2 (see above) is a yellow gas which may be liquefied, and boils at +10°. The gas and liquid are violently explosive, the substance being resolved into its elements with liberation of much heat. It is formed whenever chloric acid is set free, and hence it is seen when a little powdered potassium chlorate is touched with a drop of concentrated sulphuric acid (end of last section)*. Concentrated hydrochloric acid turns yellow from the same cause when any chlorate is added to it. These actions are used as **tests** for chlorates, and distinguish them from perchlorates (*q.v.*). With water, chlorine dioxide gives a mixture of **chlorous acid** $HClO_2$ and chloric acid, and with bases a mixture of the **chlorite** and chlorate.

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* The mixture of sugar and potassium chlorate (p. 313) can be set on fire by a drop of sulphuric acid. The latter liberates chloric acid, which in turn gives ClO_2, and the latter, being a violent oxidizing agent, starts the combustion of the sugar.

Perchlorates. — When heated, chlorates give **perchlorates.** Chlorates also give oxygen at the same time (p. 27):

$$\begin{cases} 2KClO_3 \rightarrow 2KCl + 3O_2, \\ 4KClO_3 \rightarrow 3KClO_4 + KCl. \end{cases}$$

These actions, like the three decompositions of hypochlorous acid (p. 308), are independent, and proceed simultaneously. They are **concurrent** reactions (see below). Their relative speed, however, varies with the temperature, and the decomposition into chloride and oxygen may completely outrun the other when a catalytic agent like manganese dioxide is added (p. 29). When pure potassium chlorate is heated cautiously, about one-fifth of it has lost all its oxygen by the time the rest has turned into perchlorate. The mixture may be separated by grinding with the minimum quantity of water which will dissolve the chloride it contains. The perchlorate, having at 15° less than one-twentieth of the solubility of the chloride, will remain, for the most part, undissolved. The perchlorates are much more stable (p. 93) than the chlorates, or hypochlorites: they are all soluble in water, and they are **used** in making matches and fireworks.

Perchloric Acid $HClO_4$ and Perchloric Anhydride Cl_2O_7. — Pure **perchloric acid** explodes when heated above 92°. But, like other liquids, its boiling-point is lower when its vapor *is under reduced pressure* (*cf*. p. 87). At 56 mm. pressure it boils at 39°, a temperature at which hardly any decomposition is noticeable. Hence the acid may be made by mixing potassium perchlorate and concentrated sulphuric acid and distilling the mixture cautiously in a vacuum (p. 222):

$$KClO_4 + H_2SO_4 \leftrightarrows KHSO_4 + HClO_4 \uparrow.$$

Perchloric acid is a colorless liquid, which decomposes, and often explodes spontaneously, when kept. A 70 per cent solution in water is perfectly stable; however. Although it is an active oxidizing agent, it is not so active as chloric acid, and does not oxidize hydrogen chloride in cold aqueous solution. Hence a drop of hydrochloric acid placed on a crystal of a perchlorate gives no yellow color. When the acid is liberated by concentrated sulphuric acid, it does not at once give the yellow chlorine dioxide (p. 314).

Perchloric anhydride Cl_2O_7 may be prepared by adding phosphoric anhydride to perchloric acid in a vessel immersed in a freezing mixture, $P_2O_5 + 2HClO_4 \rightarrow 2HPO_3 + Cl_2O_7$. Phosphoric anhydride is often used in this way for removing the elements of water from compounds. It combines with the water to form metaphosphoric acid HPO_3. By gently warming the mixture, the perchloric anhydride can be distilled off. It is a colorless liquid boiling at 82° (760 mm.) and exploding when struck or too strongly heated.

Relation of Anhydride and Acid or Salt. — The derivation of the formula of the anhydride from that of the acid or salt should receive special attention. In the mind of the chemist, the one always instantly suggests the other, so often does he think of them as potentially the same substance. The beginner, however, finds this habit hard to acquire, and indeed is more likely to blunder, in trying to divide the formula of an acid into the formulæ of water and the anhydride, than in any other calculation he makes.

The rule is: If the formula of the acid shows an *even* number of hydrogen atoms (H_2SO_4 or H_4SiO_4), subtract all the elements of water (H_2O or $2H_2O$), and the balance is the anhydride (SO_3 or SiO_2). The divided formulæ are H_2O,SO_3 or $2H_2O,SiO_2$. If there is an *odd* number of hydrogen atoms ($HClO_4$ or H_3PO_4) *double* the formula ($H_2Cl_2O_8$ or $H_6P_2O_8$), and subtract all the elements of water as before (Cl_2O_7 or P_2O_5). Then check the result, by adding the water again, and dividing by two, correcting the blunder if one has been made.

If the substance is a salt ($CuSO_4$ or $KClO_4$), subtract the oxide of the metal (CuO or K_2O), taking care to assign to the metal the same valence in the oxide as it shows in the salt (SO_3 or Cl_2O_7).

There are several uses for this art of ascertaining the anhydride corresponding to a given salt or acid. One is in the making of equations (see p. 325). Another is in finding the valence of the non-metal. Thus, in $KClO_4$ the anhydride is Cl_2O_7, and the valence of the chlorine is seven. In H_3PO_4 the anhydride is P_2O_5 and the phosphorus quinquivalent. In HPO_3 (metaphosphoric acid), the anhydride is again P_2O_5, and the phosphorus is therefore in the same state of oxidation — both are phosphor*ic* acids.

Simultaneous, Independent Chemical Changes in the Same Substances. — When two or more reactions go on simultaneously in the same materials, the actions may be consecutive (p. 289) or they may be parallel. In the latter case they are called **concurrent reactions.** Thus, hypochlorous acid undergoes three different changes:

$$2HClO \rightarrow H_2O + Cl_2O.$$
$$3HClO \rightarrow HClO_3 + 2HCl.$$
$$2HClO \rightarrow 2HCl + O_2.$$

Some molecules decompose into water and chlorine monoxide (p. 308), while others give chloric acid and hydrogen chloride, and still others hydrogen chloride and oxygen. Since the *same molecule* cannot undergo more than one of these different changes, it follows that the actions are independent of one another. This is shown by the fact that in sunlight the third predominates, while in the dark it falls far behind the second. Since the *relative* quantities of the products vary, the **several simultaneous actions cannot be put in the same equation.** The fundamental property of an equation is to show the *constant* proportions by weight between every pair of substances in it. Hence three separate equations are required in the present, and in all similar cases where all the proportions are not constant. Thus, again, in the decomposition of potassium chlorate by heating (p. 315), it would be misleading and wrong to add the two equations together and write, for the whole action:

$$2KClO_3 \rightarrow KCl + KClO_4 + O_2.$$

This equation would mean that the proportions amongst the products were always $KCl : KClO_4 : O_2$ or 74.6 : 138.6 : 32, whereas, in fact, the proportions vary with the conditions — the temperature used or the presence of a catalyst which hastens one action but not the other.

Consecutive reactions (p. 289), however, like (1) followed by (2) on pp. 308, 313, may be combined in one equation, since in them all the proportions must necessarily be constant. These equations are interlocked, for (2) consumes what (1) produces.

Oxygen Acids of Bromine. — No oxides of bromine have been made, but the acids $HBrO$ (hypobromous acid) and $HBrO_3$ (bromic acid) and their salts are familiar.

By the action of bromine on dilute, cold potassium hydroxide solution, **potassium bromide** and **hypobromite** are formed:

$$Br_2 + 2KOH \rightarrow KBr + KBrO + H_2O.$$

When the solution is heated, the hypobromite turns into **potassium bromate** and bromide. The actions are exact parallels of the corresponding ones for chlorine (pp. 309, 313).

Aqueous **bromic acid** $HBrO_3$ may be made in the same way as chloric acid (p. 314), or by the action of chlorine-water on bromine:

$$5HClO + H_2O + Br_2 \rightarrow 2HBrO_3 + 5HCl.$$

The solution is colorless and has powerful oxidizing properties. Thus, it converts iodine into iodic acid: $2HBrO_3 + I_2 \rightarrow 2HIO_3 + Br_2$. It appears, therefore, that iodine has more affinity for oxygen than has bromine.

The Oxide and Oxygen Acids of Iodine. — The following are the familiar acids and their corresponding salts:

HIO_3	Iodic acid,	KIO_3	Potassium iodate,
[HIO_4	Periodic acid],	$NaIO_4$	Sodium periodate,
H_5IO_6	Periodic acid,	$Na_2H_3IO_6$	Disodium periodate.

There is one oxide, iodic anhydride I_2O_5.

Sodium Iodate $NaIO_3$ is found in Chile saltpeter. It may be made, in much the same fashion as are the chlorates and bromates (pp. 313, 318), by adding powdered iodine to a hot solution of potassium or sodium hydroxide. It is disodium periodate $Na_2H_3IO_6$, however, which, being least soluble, crystallizes out.

Iodic Acid HIO_3 is formed by passing chlorine through iodine suspended in water. The action is parallel to that of chlorine on bromine-water:

$$5HClO + H_2O + I_2 \rightarrow 2HIO_3 + 5HCl.$$

A still better way is to boil iodine with aqueous nitric acid (*q.v.*). The latter gives up oxygen readily, and is here used solely on this account. Hence, it may be omitted from the equation, only the oxygen, of which it is the source, appearing:

$$I_2 + H_2O + 5O \rightarrow 2HIO_3.$$

In both these actions the initial substances (including the excess of nitric acid) and the products, with the exception of the iodic acid itself, are all volatile. When the solution is concentrated by evaporation, therefore, only the iodic acid crystallizes. It is a white solid, perfectly stable at ordinary temperatures, and can be kept indefinitely. At 170° it begins to give off water vapor ($2HIO_3 \rightleftarrows H_2O + I_2O_5$), leaving **iodic anhydride.** The latter is a white crystalline powder which may be raised to 300° before it, in turn, breaks up, giving iodine and oxygen.

Chemical Relations. — The compounds of the halogens with metals and with hydrogen diminish in stability, with ascending atomic weight of the halogen, in the order: F (19), Cl (35.5), Br (80), I (127). Each halogen will displace those following it from *this kind* of combination. In the case of the oxygen compounds, the order of stability is just the reverse, those of iodine, for example, being the only ones which are reasonably stable.

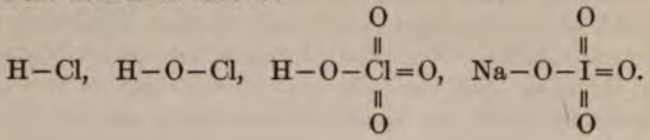
Amongst the oxygen acids of any one halogen, those containing most oxygen are most stable. The salts are in all cases more stable by far than the corresponding acids.

The halogens when combined with metals and hydrogen are univalent (HI, KCl, etc.). It is clear, however, that, when united with oxygen, their valence is higher. The maximum is shown in perchloric anhydride (Cl_2O_7), where chlorine appears to be septivalent.

The formulæ of the acids might be written so as to retain the univalence:

$$H-Cl,\ H-O-Cl,\ H-O-O-Cl,\ H-O-O-O-Cl,$$
$$H-O-O-O-O-Cl.$$

But compounds in which we are *compelled* to believe that two oxygen units are united are usually unstable (*e.g.*, hydrogen peroxide, $H-O-O-H$), and we should expect the instability would be greater with three and with four units of oxygen in combination. Here, however, the reverse state of affairs must be taken account of in our formulæ, for $HClO_4$ is the most stable of the chlorine set. This reasoning, together with the septivalence in Cl_2O_7, leads us to assume the valence seven in perchloric acid (see Periodic system) The structural formulæ (*cf.* p. 292) of some of these substances are therefore written as follows:



$$\mathrm{H{-}Cl},\quad \mathrm{H{-}O{-}Cl},\quad \mathrm{H{-}O{-}}\begin{array}{c}\mathrm{O}\\ \|\\ \mathrm{Cl}\\ \|\\ \mathrm{O}\end{array}\mathrm{{=}O},\quad \mathrm{Na{-}O{-}}\begin{array}{c}\mathrm{O}\\ \|\\ \mathrm{I}\\ \|\\ \mathrm{O}\end{array}\mathrm{{=}O}.$$

OXIDATION AND REDUCTION

Oxidation by Oxygen. — The simplest oxidations are the cases where a metal or non-metal *unites with oxygen:*

$$2Cu + O_2 \rightarrow 2CuO, \qquad S + O_2 \rightarrow SO_2.$$

Union of a compound with *additional oxygen* is oxidation also.

$$2SO_2 + O_2 \rightarrow 2SO_3, \qquad 3KClO \rightarrow 2KCl + KClO_3.$$

The *removal of hydrogen* from hydrogen chloride (preparation of chlorine, p. 156), is also defined as oxidation.

$$O_2 + 4HCl \rightarrow 2H_2O + 2Cl_2.$$
$$2KMnO_4 + 16HCl \rightarrow 8H_2O + 2KCl + 2MnCl_2 + 5Cl_2.$$

Every oxidation is accompanied by reduction of the oxidizing agent. Thus, in the second last equation, the free oxygen is reduced to water. Again, in the third last equation, 2KClO is reduced to 2KCl, while 1KClO becomes $KClO_3$ by oxidation.

In the laboratory, we frequently discover that an oxidation has occurred by noticing the presence of a product of reduction. Thus, when we heat carbon with sulphuric acid: $2H_2SO_4 + C \rightarrow CO_2 + 2H_2O + 2SO_2$, we do not notice the product of oxidation, CO_2, because it is odorless and colorless, but we perceive at once the *odor* of the sulphur dioxide, and realize that the sulphuric acid must have oxidized some substance, or this gas would not have been formed at the temperature employed.

Note that the removal of the elements of water is *neither oxidation nor reduction*, for equivalent amounts of both oxygen and hydrogen are removed:

$$2HClO \rightarrow H_2O + Cl_2O, \qquad H_2CO_3 \rightarrow H_2O + CO_2.$$

In the cases discussed above, oxidation consists always in adding oxygen or removing hydrogen.

Oxidation by Other Negative Elements. — Oxygen is only one of the class of elements called non-metallic or negative elements, so we cannot logically *restrict* the term "oxidation" to actions involving oxygen. Thus, forming a chloride, or increasing the proportion of chlorine in a compound is oxidation:

$$Cu + Cl_2 \rightarrow CuCl_2, \qquad 2FeCl_2 + Cl_2 \rightarrow 2FeCl_3.$$

In every compound, one of the elements is relatively positive and the other relatively negative. Thus, copper is positive and chlorine negative. In carbon dioxide CO_2, carbon is (relatively) positive and oxygen negative, and in calcium carbide CaC_2, calcium is positive and carbon (relatively) negative.

Thus, **oxidation is introducing, or increasing the proportion of the negative element, or removing, or reducing the proportion of the positive element.** Reduction is the converse.

Oxidation and Valence. — Combining a metal with oxygen or sulphur raises the *active valence* of the metal from zero to some finite value: $2Cu^0 + O_2{}^0 \rightarrow 2Cu^{II}O^{II}$. *Metallic* copper has *no valence in use.* In CuO or $CuCl_2$ it has gained the valence II. The copper has been oxidized. Similarly, changing $FeCl_2$ into $FeCl_3$ increases the active valence of the iron from II to III (oxidation). Conversely, changing 2HCl to Cl_2 decreases the active valence of chlorine from I to zero (oxidation). In the same equation (p. 320), KMn in $KMnO_4$ must have a total valence of VIII, but in the products $KCl + MnCl_2$ the total valence has decreased to III (reduction).

Again, in displacement, *e.g.,* $Zn + 2HCl \rightarrow ZnCl_2 + H_2$, the zinc is oxidized because the active valence goes from zero to II, and the hydrogen is reduced.

Hence, **oxidation** consists in **increasing the active valence of a positive element or decreasing that of a negative element.** Reduction is the converse.

This way of stating the rule makes it clear why removing the elements of water is neither oxidation nor reduction. We are removing *both* a positive and a negative element, and are removing them in *equi-valent* amounts, $2H^I + O^{II}$.

Oxidation and Ionization. — If, in the last illustration, we write the equation ionically: $Zn + 2H^+ \rightarrow Zn^{++} + H_2$, we discover that, logically, we must consider the change from metallic zinc to zinc-ion to be in itself oxidation. This is the case whether the zinc-ion later combines with a negative ion to form a molecule or not. Mere union or disunion of ions is neither oxidation nor reduction. Conversely, the discharge of the $2H^+$ giving H_2 is reduction.

Thus, **ionization of an elementary substance to form a positive ion is oxidation,** and **ionization to form a negative ion is reduction,** and conversely.

Oxidation and Electrons. — Increasing the valence of an atom of a positive element (oxidation) consists in removing one or more electrons: $Na^0 - \epsilon = Na^+$ (p. 235). Increasing the valence of an atom of a negative element (reduction) means adding one or more electrons: $Cl^0 + \epsilon \rightarrow Cl^-$.

Hence, **oxidation** is **removing electrons** and **reduction** is **adding electrons.**

Making Equations for Oxidations and Reductions. — The writing of equations for actions involving oxidation and reduction, *where there are more than two substances on one side of the equation,* is difficult, and a system or plan is of great value. The plan of **partial equations** (p. 194) is often helpful. There are three other systems which are in use. (1) When the action involves oxygen acids and their salts, the formulæ can be rewritten so as to **show the anhydride** (see below). (2) The second, called the system of **positive and negative valences,** is more generally applicable (next section). (3) The third describes oxidation in terms of **ions and positive electrical charges** (p. 325).

Making Equations: Using Positive and Negative Valences (p. 276). — 1. Each compound is composed of *elements* which are, relatively to one another, *either positive or negative.* Thus, in $KMnO_4$, K and Mn are positive and O is negative. In CS_2, C is (relatively) positive and S negative (see p. 277). We say, then, that C has a positive valence of four (+4) and S has a negative valence of two (−2), just as it has in H_2S.

2. *In each compound, the algebraic sum of the positive and negative valences must be zero.* Thus, in CS_2 the sum is $+4 - 2 \times 2 = 0$ ($C^{++++}S_2^{=}$). This is simply the rule of equi-valence (p. 62), with the addition of the idea of relative positiveness and negativeness.

This enables us **to determine the valence of each element in a compound like $KMnO_4$.** K^+ is always univalent and positive. $O^{=}$, in inorganic compounds, is always bivalent and negative. The valence of Mn has different values: $Mn^{II}Cl_2$, $Mn_2^{III}O_3$, $Mn^{IV}O_2$, $Mn_2^{VII}O_7$, etc. By the rule (sum of valences equals zero) we can tell the valence of Mn in this compound. The valence of O_4 ($4O^{=}$) is -8. That of K is $+1$. That of Mn must therefore be $+7$ ($KMn^{+VII}O_4$).[*] Again, in $HClO_3$, the valence of O_3 is -6, that of H is $+1$, therefore that of Cl must be $+5$. Still again, in $K_2Cr_2O_7$, the valence of O_7 is -14, that of K_2 is $+2$, that of Cr_2 is therefore $+12$, and that of Cr necessarily $+6$ ($K_2Cr_2^{+VI}O_7$).

3. Since rule 2 applies to every compound used or produced in a chemical change, it follows that when in a reaction *the valence* of an element *changes in value, that of one or more of the other elements must also change, so as to maintain the equality of + and − valences.* Thus, if one element loses in valence, to the extent of $+6$, some other element (or elements) must *lose* -6, or *gain* $+6$. The gain (or loss) of one element must cancel the gain (or loss) of some other element.

4. The *valence of a free element*, that is, its active valence, is *zero.* A free element is also *neutral* — neither positive nor negative — because it is not combined with any other element.

Illustration of rules 3 *and* 4. Thus, in the action for preparing chlorine with manganese dioxide (p. 158):

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2,$$

4H ($4H^+$) has the valence $+4$ on both sides. On the left side, 4Cl ($4Cl^-$) has the valence -4: on the right, 2Cl has the valence -2, and Cl_2 has the valence 0. So far as chlorine is concerned, there is a change from -4 to -2, or a difference of -2. Again, on the right, Mn has the valence $+2$, while on the left side it has the valence $+4$, a difference of $+2$. The two differences, -2 and $+2$, cancel one another. Stated otherwise, manganese lost +2 and chlorine lost −2, so that the other + and − valences *still in use* remained equal in number, and equi-valence was preserved.

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[*] The reader should write this, and other formulæ discussed below, so as to show the valences thus: $K^+Mn^{+++++++}O_4^{=}$ (*cf.* p. 276).

Balancing an Equation. Suppose we wish to balance the equation for the decomposition of chloric acid $HClO_3$. We ascertain, in the laboratory, that the products are perchloric acid $HClO_4$, chlorine dioxide ClO_2, and water.

Skeleton: $HClO_3 \rightarrow HClO_4 + ClO_2 + H_2O$.

Since H^+ and $O^=$ do not change in valence, only Cl has been affected. On the left side, the valences are $O_3 = -6$, $H = +1$, Cl therefore $= +5$.* On the right side, in $HClO_4$, the total valence of oxygen is −8 and of hydrogen +1. That of Cl is therefore +7. In ClO_2, the valence of O_2 is −4, and that of Cl therefore +4. Thus, Cl changes, from +5, partly to +7 and partly to +4. To achieve this, arithmetically, we require 3Cl on the left $(= 3 \times +5 = +15)$, giving $Cl = +7$ and $2Cl = 2 \times +4 = +8$, or a total of +15 on the right. Thus, we require $3HClO_3$:

Balanced: $3HClO_3 = HClO_4 + 2ClO_2 + H_2O$.

Balancing Another Equation. In the reaction for preparing chlorine (p. 157), the skeleton is:

Skeleton: $KMnO_4 + HCl \rightarrow H_2O + KCl + MnCl_2 + Cl$.

Here, in $KMnO_4$, the valence of Mn is +7. In $MnCl_2$ it is +2, a loss of +5. The chlorine also changes its valence from −1 to 0, a loss of −1. Evidently, so that the changes may cancel out, for every Mn losing +5, 5Cl must lose 5 × −1 and be liberated:

Incomplete: $KMnO_4 + HCl \rightarrow H_2O + KCl + MnCl_2 + 5Cl$.

Since there is now, altogether, 8Cl on the right, 8HCl will be required on the left. The 8H will give $4H_2O$:

Balanced: $KMnO_4 + 8HCl \rightarrow 4H_2O + KCl + MnCl_2 + 5Cl$.
Molecular: $2KMnO_4 + 16HCl \rightarrow 8H_2O + 2KCl + 2MnCl_2 + 5Cl_2$.

For another method of balancing this equation, see p. 157.

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* Write these (and other formulæ) thus: $H^+Cl^{+++++}O_3^{=}$ (*cf.* p. 276).

Making Equations, by Using the Anhydrides. — To balance the equation for the decomposition of chloric acid, we first write the skeleton equation:

Skeleton: $HClO_3 \rightarrow HClO_4 + ClO_2 + H_2O.$

Then we divide the acids into water and the anhydrides (p. 316).

Analyzed: $H_2O,Cl_2O_5 \rightarrow H_2O,Cl_2O_7 + ClO_2 + H_2O.$

We now perceive that, disregarding the water, some Cl_2O_5 must lose oxygen to give $2ClO_2 + O$, and that some Cl_2O_5 must gain $2O$, becoming Cl_2O_7. To furnish the $2O$, clearly $2Cl_2O_5$ is required, giving $4ClO_2 + 2O$, and a third Cl_2O_5 gains this $2O$. Thus, altogether $3Cl_2O_5$ will be required:

Balanced: $3H_2O,Cl_2O_5 \rightarrow H_2O,Cl_2O_7 + 4ClO_2 + 2H_2O$

or $6HClO_3 \rightarrow 2HClO_4 + 4ClO_2 + 2H_2O.$

This equation is then divided by two throughout.

Making Equations by Oxidation of Ions, Using Positive Electrical Charges. — All oxidation reactions involving ionogens can be written in terms of ions. Thus, the oxidation of hydrochloric acid by potassium permanganate can be so written. The potassium-ion clearly is not affected, and may be omitted. The ions concerned are:

$$MnO_4^- + H^+ + Cl^- \rightarrow H_2O + Mn^{++} + Cl^0.$$

Cl^0 with no charge stands for free chlorine. Now we can divide the action into (1) the behavior of the oxidizing agent, which is general, and will be used wherever the same oxidizing agent is used; (2) the fate of the substance being oxidized, which again is general, because other oxidizing agents will change it in the same way.

$$MnO_4^- + 8H^+ \rightarrow 4H_2O + Mn^{++} + 5\oplus. \qquad (1)$$

In words, each permanganate ion, with a free acid present (oxidizing mixture), will give water, manganous-ion, and a balance of five unit positive charges.

$$5\oplus + 5Cl^- \rightarrow 5Cl^0. \qquad (2)$$

$$10\oplus + 5O_2^{=} \rightarrow 5H_2O + 5O^0_2. \qquad (2^{\mathrm{I}})$$

$$10\oplus + 5SO_3^{=} + 5H_2O \rightarrow 5SO_4^{=} + 10H^+. \qquad (2^{\mathrm{II}})$$

These three equations represent the oxidation of (2) hydrochloric acid, or (2^{I}) hydrogen peroxide, giving free oxygen, or (2^{II}) sulphurous acid, with water furnishing the oxygen, and leaving the solution strongly acid ($= 5H_2SO_4$). Note that the sums of the + and − charges on opposite sides of each equation are equal.

To obtain the final ionic equation, add (1) and (2):

$$\begin{array}{rl} MnO_4^- + 8H^+ \rightarrow 4H_2O + Mn^{++} + 5\oplus. & (1) \\ 5\oplus + 5Cl^- \rightarrow 5Cl^0. & (2) \\ \hline MnO_4^- + 8H^+ + 5Cl^- \rightarrow 4H_2O + Mn^{++} + 5Cl^0. & \end{array}$$

Before adding (1) and (2^{I}) and (1) and (2^{II}), the first equation (1) must be doubled throughout, so that the $10\oplus$ may cancel out.

Exercises. — 1. Assign to its proper class (pp. 166, 258) each of the actions mentioned in this chapter.

2. Knowing that potassium fluosilicate K_2SiF_6 is insoluble, how should you make chloric acid (p. 314)?

3. Make the equation for the interaction of chlorine with calcium hydroxide in hot water (p. 313). How should you make zinc chlorate from zinc hydroxide $Zn(OH)_2$?

4. How should you make pure potassium hypochlorite from hypochlorous acid (p. 254)?

5. Explain, in terms of ionic equilibrium, why dilute hypochlorous acid can be obtained by adding one-half of an equivalent of an active acid (p. 309) to bleaching powder, and distilling the mixture.

6. On what circumstances would the possibility of making barium chlorate by action of chlorine on barium hydroxide depend (p. 313)? Could pure barium chlorate be obtained easily by this means (see Table of Solubilities)?

7. Make the equations for: (*a*) the preparation of potassium bromate; (*b*) pure aqueous bromic acid; (*c*) the interaction of iodine with aqueous potassium hydroxide in the cold, and (*d*) when heated.

8. Make the equations for the interactions of chlorine dioxide with water, and with aqueous potassium hydroxide.

9. Find the formulæ of the anhydrides of the following acids:

$$HPO_3,\quad H_2SeO_4,\quad H_3AsO_3,\quad H_3AsO_4,\quad H_6SO_6.$$

10. Find the formulæ of the anhydrides of the acids from the following formulæ of salts:

$$Na_2SiO_3,\quad Na_2HPO_4,\quad NaH_2PO_3,\quad Na_2H_3IO_6.$$

11. Classify the following changes as oxidations or reductions. (*a*) $H_2Cr_2O_7 \rightarrow H_2CrO_4 + CrO_3$; (*b*) $HMnO_4 \rightarrow MnO_2$; (*c*) $I^0 \rightarrow I^-$; (*d*) $2H_2O_2 \rightarrow 2H_2O + O_2$.

12. Using positive and negative valences, determine whether each of the following formulæ is correct or incorrect: $Ca(MnO_4)_2$, $Al(ClO_4)_3$, Na_2HIO_5.

13. Apply each of the three methods (pp. 322, 325) of writing equations to the four following reactions: (*a*) chlorine-water on bromine; (*b*) chlorine-water on hydrogen sulphide, giving free sulphur; (*c*) potassium permanganate and free acid on hydrogen sulphide, giving free sulphur; (*d*) potassium dichromate and free acid (p. 224) on hydrogen sulphide, giving the chromic salt of the acid (Cr^{III}) and free sulphur.

CHAPTER XXIV

THE ATMOSPHERE. THE HELIUM FAMILY

THE pressure which is exerted by the air upon each square centimeter of the earth's surface is 1033.6 g., or a little over one kilogram. This is nearly fifteen pounds to the square inch.

There are three classes of **components** in the air. Those of the **first** class, oxygen, nitrogen, and the inert gases of the helium family, are present in almost **constant quantities.** Those of the **second** class are very **variable in quantity,** and include carbon dioxide, water vapor, and dust. Those of the **third** class, such as the sulphur dioxide in city air, are **accidental.**

Components which are Constant in Amount. — In the determination of the **oxygen** in air, phosphorus enclosed in iron gauze (Fig. 90), may be used. The oxygen combines to form several oxygen acids of phosphorus. The volume of gas is read off before the phosphorus is introduced, and after it has been withdrawn.

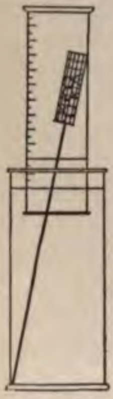
FIG. 90.

In the air taken from mines, from mountain tops, from the surface of the sea, and from inland regions, the percentages of oxygen by volume are found to be very constant (20.9 to 21.0).

When air, from which the oxygen has been removed by phosphorus, or by passage over heated copper or iron, is led slowly through a heated tube containing magnesium, the **nitrogen** unites with the metal to form the solid magnesium nitride Mg_3N_2, and only about 10 c.c. out of every liter remains uncombined. This residuum is **argon,** mixed with 0.15 per cent of its volume of other gases belonging to the helium family.

The Carbon Dioxide. — Pure country air contains about 3 parts in 10,000 of **carbon dioxide** CO_2. In city air there are from 6 to 7 parts in the same volume, while in the air of audience-rooms the proportion may rise as high as 50 parts.

The **sources** of the carbon dioxide in the air are numerous. It comes from the decay of vegetable and animal matter, in which, chiefly through the influence of minute vegetable organisms, the carbon is oxidized to carbon dioxide. It is formed also by the combustion of coal and wood, but the thirteen hundred million tons of coal burned annually, giving three times that weight of carbon dioxide, would add only one-six hundredth to the total present in the air. It is exhaled by animals, being produced in the body by oxidation of the carbon in the food which they eat. It also issues from the earth, in volcanic as well as in other neighborhoods. The proportion of this gas in the air would naturally increase continuously, though slowly, as the result of these processes, were it not that it is removed just as continuously by the action of growing plants (see p. 387), which use it as food. It may be added, also, that carbon dioxide, being a soluble gas, is contained in sea water (dissolved and as $Ca(HCO_3)_2$), and the total amount in the ocean is much greater than that in the air. The removal by plants and by sea water thus keeps the proportion in the air fairly constant.

The presence of carbon dioxide in the breath may be shown very quickly by blowing through a tube into calcium hydroxide solution (limewater). Calcium carbonate $CaCO_3$ is precipitated. We draw about 500 c.c. of air into our lungs at each breath, or half a cubic meter per hour. In the lungs, some oxygen is removed, the percentage by volume falling from 21 to 16, and we add some carbon dioxide, the proportion increasing from 0.03 in country air to about 4 per cent. A candle flame is extinguished by exhaled air, because the maintenance of such a flame requires at least 18.5 per cent of oxygen. But air will sustain life until the proportion has fallen to about 10 per cent.

To determine the proportion of carbon dioxide, a measured volume of air is bubbled slowly through a measured volume of a solution of barium hydroxide of known concentration. Barium carbonate is precipitated: $Ba(OH)_2 + CO_2 \rightarrow BaCO_3\downarrow + H_2O$, and the quantity of barium hydroxide remaining is determined by titration (p. 256).

The Water Vapor. — The proportion of water vapor is constantly changing. When the air becomes cool, as it does most often in the upper layers, the vapor condenses to droplets, forming fogs and clouds. When the condensation continues, the drops become larger and fall as rain. On the other hand, when the weather is warm, water from the soil, and from rivers, lakes, and oceans, passes into vapor and the amount in the air increases.

Humidity. — The moisture in the air is usually defined in terms of the relative humidity, the standard being the quantity required to saturate the air. The open air is never actually saturated, but, when a portion is confined in a vessel over water, it soon becomes so. The humidity is then 100 per cent. If the partial pressure of water vapor present is only half as great as the vapor pressure of water at the same temperature, the humidity is 50 per cent. The average humidity is roughly about 66 per cent.

At 18° (64.4° F.), the vapor pressure of water is 15.4 mm. Thus air saturated with moisture at 18° (100 per cent humidity) would contain 15.4/760, or about 2 per cent by volume of water vapor. If this air were cooled to 0° (32° F.), a temperature at which the vapor pressure of water is only 4.6 mm., the air could *retain* only 4.6/760, or 0.6 per cent, of moisture. The difference, amounting to 10.4 g. (10.4 c.c.) of water per cubic meter, would condense as fog or rain.

The proportion of water in a given volume of air may be measured most accurately by permitting the air to stream slowly through tubes filled with calcium chloride or phosphoric anhydride. The increase in weight of the charged tubes represents the quantity of moisture abstracted from the sample. It may also be ascertained by noting the temperature to which air has to be cooled before it becomes saturated and deposits dew (dew-point). For example, if air at 18° has to be cooled to 11° before it deposits dew, it contains water vapor at a pressure of 9.8 mm. (Appendix IV). If saturated at 18°, it would have contained water vapor at a partial pressure of 15.4 mm. The relative humidity was, therefore, 9.8/15.4, or 63.6 per cent.

Ventilation. — On a moist day, we speak of the atmosphere as "heavy" or "oppressive." The barometer, however, is lower on such days, and the pressure below the average. Moist air must be lighter than dry air, because in moist air molecules of relative weight 18 (H_2O) have been substituted for an equal number of molecules of oxygen and nitrogen with the relative weights 32 and 28. The discomfort is due to a different cause.

The oxidation of digested food carried by the blood is accompanied by liberation of heat, yet our bodies must remain at 98.6° F. (37° C.). A rise of a few tenths of a degree produces discomfort. A little of the heat is lost by radiation from the surface of the body but the real adjustment is secured by evaporation of water through the skin. The vaporization of 1 g. of water (at 100°) removes heat amounting to 540 calories (603 cal. at 37° C.). Evaporation of a single ounce ($28\frac{1}{3}$ g.) of water will therefore lower the temperature of 96.5 kilograms (168 lbs.) of water (or flesh, which is largely water) by more than two-tenths of a degree C. (nearly 0.4° F.).

The "oppressive" feeling, then, is due to the fact that the air is too nearly saturated, evaporation is being hindered (p. 90), and heat is accumulating. Hence, the relative humidity is the measure of the goodness or badness of the air of a room.

In winter, cold and therefore relatively dry air is brought into the house and heated. This makes the relative humidity very low, evaporation proceeds too fast, and discomfort follows. In summer, however, the outside air is often already nearly saturated at the temperature of the room. Unless there is a rapid change of air by ventilation, the moisture from the bodies of those in the room increases the humidity, and discomfort arises from a cause opposite to the one which produced it in winter.

It should be noted, also, that even though the air is in constant motion, the layer of air next our skin (even the exposed parts) is hindered from moving by friction. There is a **stationary layer** close to the surface, which quickly reaches the temperature of the body and becomes saturated at that temperature. The water molecules can leave this layer, and make room for others, only by *diffusion*, which is a deliberate rather than a speedy process. Now, an electric fan, although it brings no fresh, dryer air into the room, nevertheless stirs the air and blows away the moist, saturated layer next the skin. It, at least, makes this layer much thinner, and reduces greatly the distance the water molecules have to go by mere diffusion.*

* The same conception applies to **dissolving a salt**. A stationary layer of saturated solution is formed on the surface, and the molecules of the salt can

Formerly, the accumulation of carbon dioxide from the breath was blamed for the unhealthiness of unventilated rooms. The proportion found in such rooms, however, is almost never sufficient to do any harm. Then, it was imagined that traces of highly poisonous compounds were exhaled by the body. No one, however, has yet been able to prove that such poisons exist.

The aims of ventilation are, therefore, to supply fresh outside air, to keep it in motion, and to maintain a humidity that is neither too low nor too high.

Dust in the Air. — A beam of sunlight, crossing a dark room, can be seen by the light reflected from the particles of dust in the air. Some of the particles are inorganic, and consist of clay, limestone, and soot from ill-burned fuel. The organic dust may be divided into two kinds. The part which is dead includes coal dust, refuse from the streets, minute shreds of cotton, linen, hay, etc. The living dust consists of pollen grains, spores of fungi and molds, bacteria, and similar microscopic organisms. The presence of microscopic germs in the air is shown by the fact that when food has been exposed to the air, even for a few minutes, putrefaction very soon sets in. Some germs also produce disease when they land on a place where the skin has been damaged by a cut or a burn. After infection, antiseptic treatment, *e.g.*, with hydrogen peroxide, destroys the organisms. But protection, *e.g.*, with petrolatum (p. 391), until a new skin has formed, is better.

It is worth noting that natural soil contains about 100,000 micro-organisms per c.c., good, unfiltered river water from 6000 to 20,000 per c.c., and pure air only 4 or 5 per liter.

If dust were absent from the air, there would be no clouds or rain. Aitken has shown that the water vapor will *not* condense to fog in air that has been freed from dust by filtration. When moist air is cooled, the dust particles act as nuclei, round which the liquid grows at the expense of the vapor. In the absence of dust, the cooling would produce supersaturation, which would be slowly

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escape, and make room for more, only by diffusion. In liquids, this is a *very* slow process. By shaking the solid and liquid, however, the stationary layer is partly washed away. It is made thinner, so that the distance the molecules have to travel by diffusion is greatly reduced, and the whole operation is hastened.

relieved by condensation on the surfaces of houses, plants, animals, and land. Thus, in a dustless atmosphere an awning or umbrella would afford no shelter.

The formation of fog in ordinary air, and its absence in filtered air — *e.g.*, air drawn through a wide tube packed with 20–30 inches of cotton — is easily shown in a darkened room (Fig. 91). The flask contains some water to saturate the air. When suction is applied, by the mouth, to the tube *S*, the saturated air in the flask expands and is cooled.* With ordinary air, a fog, brilliantly illuminated by the beam of light, is instantly produced. Filtered air (dustless) gives no fog. On the other hand, a whiff of smoke from smoldering paper, when admitted to the flask, causes a fog (after cooling) of extraordinary denseness.

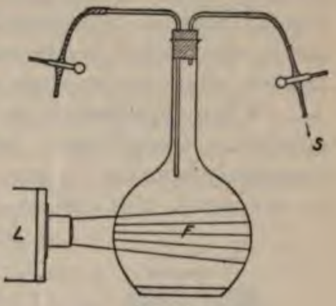

Fig. 91.

Composition of Air. — Air, when freed from carbon dioxide and water, contains by volume 78.06 per cent of nitrogen, 21.00 per cent of oxygen, and 0.94 per cent of argon. When only the water is removed, the carbon dioxide averages about 0.03 per cent of the whole.

To use an illustration of Graham's, if we imagined the air to be divided by magic into layers, all at one atmosphere pressure, and with the heavier components below, we should have: On the earth, five inches of water; above that, thirteen feet of carbon dioxide; above that, ninety yards of argon; above that, one mile of oxygen; and on the top four miles of nitrogen.

Air a Mixture. — The experiments, in which the oxygen was removed from the air and the nitrogen remained, do not prove that the original constituents were present simply in mechanical mixture. They might have been combined, and the combustion of phosphorus, for example, might have represented the removal of oxygen from combination with nitrogen and its appropriation by the phosphorus. It may be well, therefore, to point out some reasons which lead us to regard the air as a mixture:

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* Compression with a bicycle pump *heats* air, and expansion cools it.

1. Each of the substances in air has precisely the same properties which it exhibits when free, separate, and pure. This is characteristic of a mixture. Thus, the *density* of air is precisely that which we find by calculation from the known proportions and several densities of the components. Again, the *solubility* of each gas is observed to be the same as if the same amount of it were present, alone, in the same volume.

2. When liquefied air is allowed to evaporate in a suitable apparatus, the nitrogen, being more volatile, can be separated completely from the oxygen. When the oxygen, in turn, is allowed to evaporate, the carbon dioxide and water remain as solids, frozen at this low temperature.

3. Finally, the proportions by weight cannot be represented by a chemical formula, because they are not exact multiples of the atomic weights by integral numbers. This is a sure proof that it is not a *chemical* aggregate.

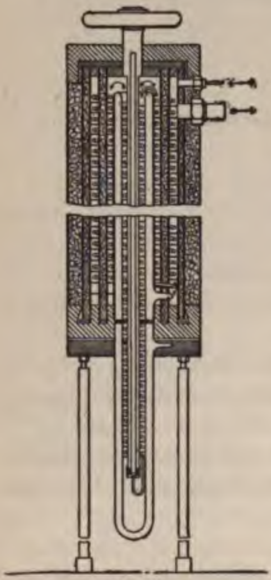


FIG. 92.

Liquefaction of Gases.—The earliest experiments of this kind were made by Northmore (1805), who liquefied chlorine, hydrogen chloride, and sulphur dioxide. In 1823 chlorine was again liquefied by Faraday. During the following years he reduced sulphur dioxide, hydrogen sulphide, carbon dioxide, nitrous oxide, cyanogen, and ammonia to the liquid condition. He failed, however with oxygen, hydrogen, and nitrogen. In 1883 Wroblevski and Olszevski prepared visible amounts of liquid oxygen. About the same time Dewar devised means of manufacturing large quantities of liquid air and oxygen. The most successful apparatus for use on a small scale is that devised by Hampson.

In Hampson's apparatus (Fig. 92), two concentric copper pipes, about 130 meters in length, are coiled closely in a cylindrical form, with non-conducting covering to prevent access of heat. Air at 130–150 atmospheres pressure is forced through the inner pipe. When it reaches the extremity of this pipe, it suddenly escapes into a closed vessel. This expansion lowers its temperature. The air can now escape only by traveling back through the outer pipe to the final exit near the top. In doing so, it cools the highly compressed air in the inner pipe. This cooler air, on reaching the closed vessel, expands and becomes colder than ever, and in passing backwards lowers the temperature of the air in the inner pipe still further. Finally, the air in this pipe liquefies, and drops of liquid air are expelled into the closed vessel. They are allowed to run out through a valve, from time to time, as they accumulate.

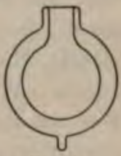


FIG. 93.

The cooling on expansion depends upon the imperfection (p. 78) of the gas, and is due to the work done in overcoming the tendency to cohesion of its molecules. Liquid air can be kept in Dewar flasks (Fig. 93). The space between the inner and outer flasks is evacuated, so that there is no gas to carry heat to the liquid air. The inner surface of the outer flask is often silvered, so that radiant heat, from surrounding bodies, may be reflected and not absorbed.

Liquid Air. — Liquid air varies in composition, as the nitrogen (b.-p. −194°) is less condensible than the oxygen (b.-p. −181.4°). It boils at about −190°, and contains about 54 per cent of oxygen by weight, while air contains 23.2 per cent. By allowing evaporation to go on, a liquid containing 75 to 95 per cent of oxygen is easily obtained (*cf.* p. 26). The gas secured by the evaporation of the residue is pumped into cylinders and sold as compressed oxygen. It contains about 3 per cent of argon, and is a convenient source of this element. Cartridges made of granular charcoal and cotton waste, when saturated with liquid air, have been used as an explosive in mining.

THE HELIUM FAMILY

Argon A. — Cavendish (1785) sought for other gases in air by adding more oxygen, passing an electric discharge to cause this gas to combine with the nitrogen, and absorbing the product (NO_2) in potassium hydroxide solution. He found that only about 0.8 per cent of inactive gas remained. Since the quantity was so small, and the spectroscope, by which the gas even in small amounts would have been recognized to be new, was not invented until much later, he did not pursue the subject.

A century later, Lord Rayleigh observed that, while specimens of oxygen and other gases made purposely from various sources always had the same density, nitrogen was an exception. One liter of nitrogen made from air, and supposed to be pure, weighed 1.2572 g. When the gas was manufactured by decomposition of five different compounds, such as urea and certain oxides of nitrogen, the mean weight of a liter of this nitrogen was only 1.2505 g. The difference, amounting to nearly 7 mgm., was very much greater than the experimental error. The suspicion naturally arose that some heavier gas was present in natural nitrogen. Soon after (1894), Rayleigh repeated Cavendish's experiment, and obtained argon. Working in coöperation with him, Professor, now Sir William Ramsay, obtained the same gas by removal of the greatly preponderating nitrogen by means of magnesium (p. 328). The new gas had a molecular weight of about 40, and was therefore more than one-third heavier than nitrogen.

The exact density of argon is 39.88. When liquefied it boils at −186.9°, and the colorless solid melts at −189.5°. The solubility of the gas in water (4 volumes in 100) is two and one-half times that of nitrogen. It has not been found to enter into any sort of chemical combination, and was named argon on this account (Gk., *inactive*). The physical properties show that the molecules of the gas, like those of mercury (p. 111), are monatomic.

Helium He.—In 1868 Lockyer first detected an orange line in the spectrum of the sun's prominences which was not given by any terrestrial substance then known. The line was so conspicuous that it was attributed to the presence of a new chemical element, which was named **helium** (Gk., *the sun*). Ramsay, in searching for sources of argon, examined a gas which Hillebrand had obtained from uraninite, an ore of uranium. He was surprised to find (1895) that it contained a large proportion of a very light gas, the spectrum of which was identical with that of solar helium. The same gas is found in small amount in the atmosphere. Helium does not exhibit any tendency to enter into combination.

It is monatomic and its density shows that its molecular weight is 4. When liquefied by Onnes, it boiled at −268.5° (4.5° Abs.).

Neon Ne, Krypton Kr, and Xenon Xe. — By liquefying atmospheric argon, using liquid air to cool it, and distilling the liquid, Ramsay (1898) found that it contained helium, along with three new gases. These together constituted one-six hundredth part of the whole. The gases were named neon (Gk., *new*), krypton (Gk., *hidden*), and xenon (Gk., *stranger*). These gases are all entirely inactive chemically, and are all monatomic. Their molecular weights are: Neon, 20.2; krypton, 82.9; xenon, 130.2 **Niton** Nt (radium emanation, *q.v.*), molecular weight 222.4, also belongs to this family.

Exercises. — 1. A sample of moist air, confined over water at 15° and 760 mm., occupies 15 c.c. It is mixed with 20 c.c. of hydrogen, and the mixture is exploded, and suffers a contraction of 9.5 c.c. What would be the volume of the oxygen it contained if measured dry at 0° and 760 mm.?

2. Calculate, from the data on p. 333 and the densities, the percentage by weight of the three principal components of air.

3. Of the proofs that air is a mixture (p. 333), which show that *no part* of the components is combined, and which that the components are not *wholly* combined?

4. What is the relation between heavier clothing and the stationary layer of air next the skin?

5. From the data given on p. 330, calculate the weight of water vapor in 1 cubic meter of air saturated at 18° and at 0°, respectively.

CHAPTER XXV

NITROGEN AND AMMONIA

NITROGEN was recognized to be a distinct substance by Rutherford (1772), Professor of Botany in the University of Edinburgh, who named it mephitic air. Scheele showed that it was present in the atmosphere. Lavoisier recognized it to be an element, and named it *azote* (Gk., *without life*) because it did not support life. The English name records the fact that it is an important constituent of niter KNO_3.

The Chemical Relations of the Element Nitrogen. — In compounds with hydrogen and the metals nitrogen is trivalent, while in those containing oxygen and other negative elements, it is frequently quinquivalent. It is a non-metal, for its oxides are acidic (p. 94). Many of the compounds of nitrogen are extremely active and interesting. Those of them which we have to discuss in inorganic chemistry are ammonia NH_3 and nitric acid HNO_3, and several related substances.

Occurrence. — Free nitrogen is present in the air. The nitrates of potassium and sodium are found in Bengal and Chile, respectively. Natural manures, such as guano, contain large quantities of nitrogen compounds, and owe their value as fertilizers to this fact. Nitrogen is a constituent of the proteins (about 15 per cent nitrogen) of vegetable and animal matter.

Preparation. — Nitrogen containing about one per cent of argon is obtained by burning phosphorus in air, or by passing air over heated copper: $2Cu + O_2 \rightarrow 2CuO$. For commercial purposes, it is obtained by evaporation of liquid air.

Pure nitrogen is prepared by heating ammonium nitrite:

$$NH_4NO_2 \rightarrow 2H_2O + N_2.$$

In practice, since ammonium nitrite is unstable and cannot be kept as such, strong solutions of ammonium chloride and sodium nitrite are mixed, a double decomposition results in the formation of ammonium nitrite, $NH_4Cl + NaNO_2 \rightleftarrows NH_4NO_2 + NaCl$, and this breaks up when heat is applied, giving nitrogen.

We may also prepare nitrogen by the oxidation of ammonia NH_3, passing the latter over heated cupric oxide (see p. 343), or by the reduction of nitric oxide NO, passing this gas over heated copper.

Physical Properties. — Nitrogen is a colorless, tasteless, odorless gas, as we should expect from the fact that air possesses these properties. It forms a colorless liquid, boiling at −194°, and a white solid (m.-p. −214°). The solubility in water (1.6 vols. in 100) is less than that of oxygen. The density of the gas shows the formula of free nitrogen to be N_2.

Chemical Properties. — Nitrogen **unites** with few elements directly. At ordinary temperatures it is almost absolutely indifferent. When passed over heated lithium, calcium, magnesium, or boron, it forms **nitrides**, in which it is trivalent. These have the formulæ Li_3N, Ca_3N_2, Mg_3N_2, and BN, respectively. Thus, when magnesium is burned in the air, the white mass which is formed contains magnesium nitride, along with much of the oxide. When the ash is moistened with water in a covered vessel, ammonia can be smelt and can be detected with moist litmus paper. The nitride is hydrolyzed:

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3\uparrow.$$

Nitrogen combines with difficulty with hydrogen to form ammonia NH_3 and with oxygen to form nitric oxide. The actions will be discussed under the compounds themselves.

One case of direct union of nitrogen is of economic importance. The supply required by most plants is obtained from nitrogen compounds contained in fertilizers, or equivalent substances already present in the soil. With the *leguminosæ* (peas, beans, clover, etc.), however, are found associated certain bacteria, which flourish in nodules upon their roots. These bacteria have the power of taking free nitrogen from the air, which penetrates the soil, and producing proteins. The nodules often contain over five per cent of combined nitrogen. The proteins, by the action of nitrifying bacteria, give nitric acid which, with bases in the soil, gives nitrates. These are soluble, and are absorbed through the roots, furnishing the nitrogen needed by plants to enable them to construct the proteins they require.

Compounds of Nitrogen and Hydrogen. — The commonest and longest known of these substances is ammonia NH_3, which was first described by Priestley (1774) and named "alkaline air." Curtius discovered hydrazine N_2H_4 in 1889, and hydrazoic acid HN_3 in 1890. Hydroxylamine $HONH_2$, discovered by Lossen in 1865, is similar to ammonia in chemical behavior.

AMMONIA NH_3

Ammonia is of interest, commercially, because large amounts of liquefied ammonia are used in refrigeration, because much is employed in the manufacture of carbonate of soda, and because its compounds are used as fertilizers.

Manufacture. — Ammonia is formed when proteins are heated in the absence of air. Thus, it was formerly obtained by the distillation of hoofs, hides, and horns, and the solution in water was called "spirit of hartshorn." Coal contains about 1 per cent of combined nitrogen, derived from the proteins of the original plants. Hence, when coal is distilled in the manufacture of coal gas or, on a much larger scale, for the making of coke, much ammonia can be secured by washing with water the gases which are given off. The solution is separated from the tar, lime is added to combine with acids, and the ammonia gas is driven out by heating and passed into sulphuric acid or hydrochloric acid. It gives ammonium sulphate or chloride (see below).

In Germany 80 per cent (1910) of the coke is made in "by-product" coke ovens, in which the ammonia and other by-products are collected and utilized; in the United States 83 per cent of the coke is made in "beehive" ovens, in which the vapors are simply burned. Ammonium sulphate is a valuable fertilizer and in 1911, in the United States, ammonia capable of yielding 400,000 tons of ammonium sulphate worth 24 million dollars was burned by the cokemakers.

The distillation of coal is the chief source of commercial ammonia. In Scotland, however, oil-bearing shale is distilled to obtain petroleum, and much ammonia, liberated at the same time, is collected. Formerly it was allowed to escape but, in the absence of a protective tariff, the competition of American and Russian petroleum compelled economy. Now, the profit on the ammonium sulphate pays the whole cost of mining and distilling the shale.

Synthetic Ammonia. — The Badische Company is now manufacturing ammonia on a large scale, for the preparation of explosives, by the direct union of nitrogen and hydrogen.

$$N_2 + 3H_2 \rightleftarrows 2NH_3 + 2 \times 12{,}200 \text{ cal.}$$

No union occurs at low temperatures and, on the other hand, the action is reversible and exothermal, so that at 700° ammonia is decomposed almost completely (Van't Hoff's law, p. 188). It is necessary, therefore, to use a lower temperature and a contact agent — such as specially prepared iron — to hasten the action. Then, too, the reaction is accompanied by a diminution in volume (4 vols. → 2 vols.), and is therefore assisted by using the gases under a pressure of 185–200 atmospheres (Le Chatelier's law, p. 190). At 500°, with these conditions, about 8 per cent of the gases combine. The ammonia is dissolved out with water, and the uncombined gases are sent through the process again. The required hydrogen may be obtained by one of the commercial processes (p. 56), and the nitrogen from liquid air.

Preparation in the Laboratory. — 1. A mixture of slaked lime and some salt of ammonium, such as ammonium chloride, either with or without water, is heated in a flask or retort provided with a delivery tube:

$$Ca(OH)_2 + 2NH_4Cl \leftrightarrows CaCl_2 + 2NH_4OH \rightleftarrows 2NH_3 + 2H_2O.$$

The ammonium hydroxide, formed by the double decomposition, immediately decomposes.

2. Warming the aqueous solution gives a steady stream of the gas. Since the gas is very soluble in water, it is collected over mercury or in an inverted jar by downward displacement of air. In both methods of preparation, it is dried with quicklime (p. 475).

Physical Properties. — Ammonia is a colorless gas with a pungent, characteristic odor familiar in smelling-salts. The G.M.V. of the gas weighs 17.26 g., so that the density is little more than half that of air (*cf.* p. 101). When liquefied it boils at −33° and the solid is white and crystalline (m.-p. −77°). One volume of water dissolves 1300 volumes of the gas at 0°, and 783 volumes at 16°. The 35 per cent solution, sold as "concentrated ammonia," has a sp. gr. 0.881. The whole of the dissolved gas may be removed by boiling (*cf.* p. 145).

Liquefied ammonia is used in refrigeration. In evaporating at −33° it absorbs 330 cal. per gram. Water alone has a greater heat of vaporization. The large amount of heat is, in both cases, required because of the relatively large volume of the vapor (due to low molecular weight) and to the fact that both liquids are associated (p. 206), and the complex molecules $(NH_3)_2$ and $(NH_3)_3$ have to be decomposed. To freeze 1 gram of water at 0°, 79 cal. have to be removed. Thus 1 g. of liquid ammonia will convert 4 g. of water into ice. Fig. 94 shows one arrangement diagrammatically. The ammonia gas, obtained from a cylinder of liquid ammonia, is driven by the pump *F* along the tube *E* and is liquefied in the tube coiled in the tank *AB*. Cold water circulating through *AB* removes the heat produced by the compression and liquefaction of the gas. The liquid ammonia is allowed to drip through the stopcock *G* into the lower coil, and there it evaporates. In doing so, it takes heat from a 30 per cent solution of calcium chloride in water. This cooled brine leaves the tank at *D*, circulates through another tank, in

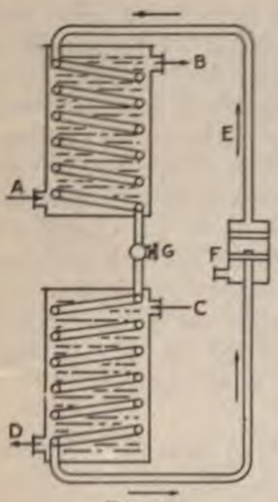


FIG. 94.

which water-filled ice molds are suspended, and returns to *C*. When used for cooling storage-rooms for meat, the brine circulates through pipes in the same way. The machine is constructed of iron, because copper and brass are corroded by ammonia.

Chemical Properties. — Ammonia, as we have seen, is **not stable,** and decomposes almost completely at 700°. A discharge of sparks from an induction coil (temperature about 2000°) has the same effect, so that a sample of the gas, confined over mercury in a closed tube (Fig. 95), may be shown to double in volume. Every two molecules give four:

$$2NH_3 \rightleftarrows 3H_2 + N_2.$$

That, even at this temperature, the action, being reversible, is still incomplete, can be shown by introducing a few drops of dilute sulphuric acid. The trace of ammonia remaining combines with this acid, forming $(NH_4)_2SO_4$ in solution. If the discharge is continued, further traces of ammonia are formed and absorbed, until, finally, the whole gas disappears.

Ammonia **reduces** many oxides, when the latter are heated and the gas is led over them:

$$3CuO + 2NH_3 \rightarrow 3Cu + 3H_2O + N_2.$$

Ammonia burns in pure oxygen (not in air) to give steam and nitrogen.

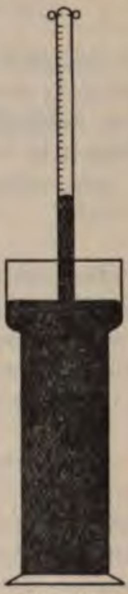


FIG. 95.

Chlorine and bromine (vapor) combine with the hydrogen and liberate nitrogen:

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl.$$

When **metals** capable of uniting with nitrogen (p. 339) are heated in a stream of ammonia gas, hydrogen is displaced. Magnesium gives magnesium nitride:

$$2NH_3 + 3Mg \rightarrow Mg_3N_2 + 3H_2.$$

Sodium and potassium, however, give amides (compounds containing the group NH_2), such as sodamide $NaNH_2$:

$$2NH_3 + 2Na \rightarrow 2NaNH_2 + H_2.$$

The most striking property of ammonia is that it **combines with acids,** giving ammonium salts:

$$\begin{array}{l} \mathrm{NH_3\,(gas) + HCl\,(gas) \;\;\rightarrow NH_4Cl\ (solid).} \\ \mathrm{2NH_3\,(gas) + H_2SO_4\,(liq.) \rightarrow (NH_4)_2SO_4\ (solid).} \end{array}$$

It **combines also with water** at or below $-79.3°$ to give ammonium hydroxide, a white solid:

$$\mathrm{NH_3 + H_2O \rightarrow NH_4OH.}$$

As the solid dissociates above $-79.3°$, a solution of the substance, which is contained in the aqueous solution of ammonia, is the only available form of ammonium hydroxide. In solution, it is a weak base.

Ammonium oxide $(NH_4)_2O$, a solid, can also be formed below $-78.6°$.

Ammonium Compounds. — Since NH_4 plays the part of a metallic element, entering into the composition of a base and of a series of salts, it is named **ammon*ium*.** As this radical forms a univalent, positive ion NH_4^+ and gives a distinctly alkaline base, it is classed with the metallic elements of the alkalies (*q.v.*).

Ammonium Hydroxide. — Although less completely ionized than potassium hydroxide, ammonium hydroxide affects litmus easily. In a normal solution, 0.4 per cent of the ammonia is in the form of ammonium-ion NH_4^+. When an acid is added to the solution, the equally small amount of hydroxide-ion which exists in it is removed and the various equilibria are displaced forward. The final result is the same as with any other base:

$$\mathrm{NH_3(gas)} \leftrightarrows \mathrm{NH_3(dslvd)} + \mathrm{H_2O} \rightleftarrows \begin{array}{r} \mathrm{NH_4OH} \leftrightarrows \mathrm{NH_4^+ + OH^-} \\ \mathrm{HCl} \leftrightarrows \mathrm{Cl^- \;\;+\;\; H^+} \end{array}\!\!\Big\} \leftrightarrows \mathrm{H_2O.}$$

Only a small proportion of the gas (one-third) is actually combined at any one time, the greater part being simply dissolved.

The solution is sold as **household ammonia,** and is used, in washing and cleaning, to soften the water.

Salts of Ammonium. — When strongly heated, all ammonium salts are decomposed and many, *but not all,* give ammonia and the acid. When the latter is volatile, the whole material of the salt is thus converted into gas. The acid and the ammonia reunite to form the solid salt when the vapor reaches a cool part of the tube (sublimation, p. 199):

$$NH_4Cl\text{ (solid)} \rightleftarrows NH_4Cl\text{ (gas)} \rightleftarrows HCl + NH_3.$$

The **test** for ammonium salts is to warm them, dry or in solution, with a base, when the *odor of ammonia* becomes noticeable.

$$\left.\begin{array}{r} (NH_4)_2SO_4 \leftrightarrows SO_4{}^{=} + 2NH_4{}^{+} \\ 2KOH \leftrightarrows 2K^{+} + 2OH^{-} \end{array}\right\} \leftrightarrows 2NH_4OH \rightleftarrows 2H_2O + 2NH_3\uparrow.$$

When the solution is used, it is the tendency of the $NH_4{}^+$ and OH^- to unite to form the slightly ionized, molecular hydroxide that sets the other equilibria in motion.

In ammonium salts, the nitrogen is quinquivalent.

Hydrazine N_2H_4. — By reduction of a compound of nitric oxide and potassium sulphite by means of sodium amalgam,* a solution of hydrazine hydrate is obtained:

$$K_2SO_3,2NO + 3H_2 \rightarrow N_2H_4,H_2O + K_2SO_4.$$

When the hydrate is distilled with barium oxide, under reduced pressure, hydrazine is liberated:

$$N_2H_4,H_2O + BaO \rightarrow N_2H_4\uparrow + Ba(OH)_2.$$

Hydrazine hydrate freezes at about −40° (b.-p. 118.5°). Its aqueous solution is alkaline, and salts are formed by neutralization.

Hydrazoic Acid HN_3. — When nitrous oxide (*q.v.*) is led over sodamide at 200°, water is liberated and sodium hydrazoate remains behind:

$$NH_2Na + N_2O \rightarrow NaN_3 + H_2O.$$

A dilute solution of the free acid is best obtained by distilling the lead salt with dilute sulphuric acid.

The pure acid (b.-p. 37°) is violently explosive, resolving itself into nitrogen and hydrogen with liberation of much heat:

$$2HN_3,Aq \rightarrow H_2 + 3N_2 + Aq + 2 \times 61,600\text{ cal.}$$

---

* The sodium dissolved in the mercury interacts with the water, giving hydrogen (see Active state of hydrogen).

Halogen Compounds of Nitrogen. — When ammonium chloride solution is treated with excess of chlorine, drops of an oily liquid, **nitrogen trichloride,** are formed: $3Cl_2 + NH_4Cl \rightarrow NCl_3 + 4HCl$. It is extremely explosive, resolving itself into its constituents with liberation of much heat.

When a solution of iodine in potassium iodide solution (p. 200) is added to aqueous ammonia, a brown precipitate is formed. This seems to have the composition NH_3,NI_3, and is named **nitrogen iodide.** It may be handled while wet. When dry, if touched with a feather, it decomposes into its constituents with violent explosion.

Exercises. — 1. When moist air is used as a source of nitrogen, what advantage is there in using copper rather than the less expensive metal iron, for removing the oxygen (p. 60)?

2. How many grams of water at 0° could be frozen (p. 85) by the removal of the heat required to evaporate 50 g. of liquid ammonia?

3. How many grams of ammonia are contained in 1 l. of "concentrated ammonia" (p. 342)?

4. What are the ions of hydrazine hydrate? Formulate (p. 254) the neutralization of this base with sulphuric acid.

5. What is the object attained by distilling under reduced pressure in making hydrazine (p. 345)?

6. Classify (pp. 166, 258), (*a*) the interaction of a nitride with water (p. 343) and (*b*) of chlorine and ammonium chloride (p. 343), (*c*) the results of heating ammonium nitrite (p. 338) and (*d*) ammonium chloride (p. 345).

7. Why does not ammonia burn in air (p. 343)?

8. What substances are present in ammonium hydroxide solution? When the liquid is heated, what happens to each? Formulate the system.

CHAPTER XXVI

OXIDES AND OXYGEN ACIDS OF NITROGEN

THE names and formulæ of the oxides and oxygen acids of nitrogen are as follows:

Nitrous oxide N_2O ⟵ Hyponitrous acid $H_2N_2O_2$
Nitric oxide NO
Nitrous anhydride N_2O_3 ⟷ Nitrous acid HNO_2
Nitrogen tetroxide N_2O_4 and NO_2
Nitric anhydride N_2O_5 ⟷ Nitric acid HNO_3.

All the oxides are endothermal compounds (p. 174), yet, with the exception of the third and the last, they are all relatively stable. The acids, when deprived of the elements of water, yield the oxides opposite which they stand (p. 281, footnote). Conversely, excepting in the case of nitrous oxide, the anhydrides with water give the acids. All of these substances are made directly or indirectly from nitric acid — nitric anhydride by removal of water, the others by reduction. We turn, therefore, first, to nitric acid and its properties. This acid is made from Chile saltpeter (next section) and also by fixation of atmospheric nitrogen (see p. 352).

NITRIC ACID HNO_3

Sources. — Sodium nitrate, or Chile saltpeter (caliche) is found in a desert region near the boundary of Chile and Peru. The deposit is about 5 feet thick, 2 miles wide, 220 miles long, and contains 20 to 60 per cent of the salt. Purification is effected by recrystallization. Potassium nitrate, or Bengal saltpeter, is found in the soil in the neighborhood of cities in India, Persia, and other oriental countries. It arises from the oxidation of animal refuse to nitric acid, through the mediation of nitrifying bacteria. The potash and lime in the soil, along with the nitric acid, give nitrates of potassium and calcium. The aqueous extract of this soil is treated with wood ashes, which contain potash K_2CO_3. It is poured off from the calcium carbonate thus precipitated, and is finally evaporated. In guano (excreta of sea birds), used as a fertilizer, the nitrogen compounds have often been converted largely into nitrates in the same way.

Manufacture. — When any nitrate is treated with any acid, nitric acid is formed by a reversible double decomposition. As sodium nitrate is the cheapest salt of nitric acid, it is always employed. For the same reason and, above all, because of its relative involatility, sulphuric acid is used to displace it:

$$NaNO_3 + H_2SO_4 \leftrightarrows NaHSO_4 + HNO_3\uparrow.$$

The nitric acid is rather volatile (b.-p. 86°), while sulphuric acid (b.-p. 330°) is much less so, and the two salts are not volatile at all. The materials are heated in cast-iron stills, and the nitric acid vapor is condensed in glass pipes surrounded by water. Thus the interaction proceeds to completion very easily (*cf.* p. 142; see also p. 185).

Physical Properties. — Nitric acid is a colorless, mobile liquid (sp. gr. 1.52) boiling at 86°, and freezing to a solid (m.-p. $-47°$). It fumes strongly when its vapor issues into moist air (*cf.* p. 144). An aqueous solution containing 68 per cent of the acid boils at 120.5°, while the pure acid, pure water, and all other mixtures, boil at lower temperatures. This 68 per cent nitric acid of constant boiling-point (p. 145) forms the "concentrated nitric acid" of commerce (sp. gr. 1.41).

Chemical Properties. — 1. Like chloric acid (p. 314), and other oxygen acids of the halogens, nitric acid is most stable when mixed with water. The pure (100 per cent) acid **decomposes** while being distilled:

$$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2,$$

yet not with explosive violence like chloric acid. The distillate is colored brown by dissolved nitrogen tetroxide NO_2 ("fuming" nitric acid). Repeated distillation finally leaves 68 per cent of the acid, mixed with 32 per cent of water formed by the above decomposition. The acid of constant boiling-point is, therefore, reached, as usual, from more concentrated as well as from less concentrated specimens.

2. Nitric acid, when dissolved in water, is highly ionized, and is therefore active as an **acid.** By interaction with hydroxides and oxides it forms nitrates.

3. When pure nitric acid (b.-p. 86°) is poured upon phosphoric anhydride, the latter combines with the elements of water, and distillation gives **nitric anhydride:** $2HNO_3 + P_2O_5 \rightarrow N_2O_5\uparrow + 2HPO_3$. The anhydride is a white solid melting at 30° and boiling at 45°. It unites vigorously with water to form nitric acid. It decomposes spontaneously into nitrogen tetroxide and oxygen: $2N_2O_5 \rightarrow 4NO_2 + O_2$.

4. Like the unstable oxygen acids of the halogens, nitric acid is an **oxidizing agent** even when diluted with water. The multiplicity of the products into which it may be decomposed by reduction, however, renders separate treatment of this property necessary (see p. 354).

5. Nitric acid interacts energetically with many compounds of carbon to give **nitro-derivatives.** Thus, when heated with phenol $C_6H_5(OH)$ (carbolic acid) it gives **picric acid** (trinitrophenol) $C_6H_2(NO_2)_3(OH)$, which crystallizes in yellow needles in the mixture. This is a yellow dye, used also as an explosive.

$$C_6H_5(OH) + 3HONO_2 \rightarrow C_6H_2(OH)(NO_2)_3 + 3H_2O.$$

When heated with toluene $C_6H_5CH_3$, it gives **trinitrotoluene:**

$$CH_3C_6H_5 + 3HONO_2 \rightarrow CH_3C_6H_2(NO_2)_3 + 3H_2O.$$

This substance (T.N.T.) is used for filling "high explosive" shells, because it can be melted (m.-p. 81.5°) and poured in, making the filling easy, safe, rapid, and complete. It is not easily exploded by shocks during transportation, but it explodes instantaneously and completely with a detonator. The following equation shows, roughly, the decomposition, and the large amount of carbon set free explains the black smoke produced:

$$2CH_3C_6H_2(NO_2)_3 \rightarrow 5H_2O + 3N_2 + 6CO_2 + 8C.$$

6. Organic compounds of another class, the alcohols (*q.v.*), interact with molecular nitric acid in a different way. The latter is mixed with sulphuric acid, which assists in the removal of the ele-

ments of water (p. 286). Thus, when glycerine is added slowly to the cooled mixture, glyceryl nitrate (so-called **nitroglycerine**) is produced:

$$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(NO_3)_3 + 3H_2O.$$

Guncotton is made by this action, cotton (cellulose) being employed:

$$(C_6H_{10}O_5)_2 + 6HNO_3 \rightarrow C_{12}H_{14}O_4(NO_3)_6 + 6H_2O.$$

7. Nitric acid produces substances of bright-yellow color, known as **xanthoproteic acids,** when it comes in contact with proteins, *e.g.*, in the skin, or in wool. Hence nitric acid stains woolen clothing yellow. This reaction is used as a test for proteins.

Nitrates. — The nitrates are all more or less easily soluble in water. When heated they decompose in one or other of three ways (see pp. 351, 356, 357). The individual nitrates, such as sodium nitrate and potassium nitrate, are described elsewhere.

NITRIC OXIDE AND NITROGEN TETROXIDE

Preparation of Nitric Oxide NO. — Pure nitric oxide is obtained by adding nitric acid to a boiling solution of ferrous sulphate in dilute sulphuric acid or of ferrous chloride in hydrochloric acid:

$$\begin{array}{rlr}
2FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3\,(+\,2H) & \times\ 3. & (1)\\
(3H) + HNO_3 \rightarrow NO + 2H_2O & \times\ 2. & (2)\\
\hline
\multicolumn{2}{l}{6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O.} &
\end{array}$$

The first partial equation does not take place at all unless an oxidizing agent like nitric acid is present (p. 225). The multiplication of the two partial equations by 3 and 2, respectively, is required in order that the hydrogen, which is not a product, may cancel out. This action is used as a means of determining the quantity of nitric acid in a solution, or of nitrates in a mixture, by measurement of the volume of nitric oxide evolved.

As we shall see (p. 354), nitric oxide may also be obtained when sufficiently dilute nitric acid (sp. gr. 1.2) acts upon copper. This interaction furnishes the most convenient method of generating the gas in the laboratory (see also p. 352).

Properties of Nitric Oxide. — Nitric oxide is a colorless gas. In solid form it melts at −167°, and the liquid boils at −153.6°. Its solubility in water is slight. The density of the gas shows the formula to be NO; and there is *no* tendency to form a polymer, such as N_2O_2, even at low temperatures.

This gas is the most stable of the oxides of nitrogen. Vigorously burning phosphorus continues to burn in the gas, nitrogen being set free. Burning sulphur and an ignited taper, however, are extinguished.

Nitric oxide has two characteristic chemical properties. It unites directly with oxygen in the cold to form the reddish-brown nitrogen tetroxide:

$$2NO + O_2 \rightleftarrows 2NO_2.$$

The same result follows when it is led into warm concentrated nitric acid: $NO + 2HNO_3 \rightleftarrows 3NO_2 + H_2O$.

It also unites with a number of salts, the compound in the case of ferrous sulphate, $FeNO.SO_4$, being capable of existence in solution and possessing a brown color. Since ferrous sulphate will first reduce nitric acid to nitric oxide (p. 350), and the excess of the salt will then give a brown color with the product, a delicate test for nitric acid is founded upon these actions.

Preparation of Nitrogen Tetroxide NO_2. — This substance is liberated by heating nitrates, other than those of potassium, sodium, or ammonium, such as lead and copper nitrates:

$$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2.$$

The oxide of the metal remains, unless this oxide is itself decomposed by heating (p. 60). When the mixed gases are led through a U-tube immersed in ice, the tetroxide condenses as a yellow liquid (b.-p. 22°, m.-p. −10.5°), and the oxygen passes on.

The compound may also be made by direct union of nitric oxide and oxygen, or by oxidation of nitric oxide by concentrated nitric acid (p. 351). It is likewise almost the sole product of the interaction of *concentrated* nitric acid with tin or copper (see p. 355). If any nitric oxide were produced by the primary action, it would be oxidized to nitrogen tetroxide in passing up through the acid (p. 351).

Properties of Nitrogen Tetroxide. — The most striking peculiarity of this gas is that, when hot, it is deep brown in color, and when cold, pale yellow. The density of the brown gas, at 140°, corresponds to the formula NO_2, that of the yellow gas at 22°, to N_2O_4. When the temperature is carried above 154°, by passing the brown gas through a red-hot tube, the brown color disappears, and nitric oxide and oxygen are formed. On cooling, the same steps through brown gas to pale-yellow gas are retraced:

$$\underset{\text{Colorless}}{2NO + O_2} \rightleftarrows \underset{\text{Brown}}{2NO_2} \rightleftarrows \underset{\text{Colorless}}{N_2O_4}$$

Since nitrogen tetroxide yields free oxygen more readily than does nitric oxide, phosphorus burns readily in it; a taper, however, is extinguished. On account of its oxidizing power, it is sometimes used in bleaching flour.

This oxide is intermediate in composition between nitrous and nitric anhydrides, and, when dissolved in *cold* water, gives *both* nitric and nitrous acids: $N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$. If a base is present, a mixture of the nitrate and nitrite of the metal is produced. When the water is not cooled, the nitrous acid (*q.v.*), being unstable, gives nitric oxide and nitric acid: $3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO$.

NITRIC ACID FROM ATMOSPHERIC NITROGEN

The Reactions Involved. — Nitrogen and oxygen have no tendency to unite at room temperature to form nitric oxide. The union is endothermal, and is therefore favored by a high temperature (Van't Hoff's law, p. 188):

$$N_2 + O_2 + 43{,}200 \text{ cal.} \rightleftarrows 2NO.$$

Even at 2000°, however, using atmospheric air, only 1 per cent of nitric oxide is formed, and at 3000°, 5 per cent. The electric discharge actually used gives about 1 per cent.

The mixture is next *cooled*, to permit the union of $2NO + O_2 \rightleftarrows 2NO_2$, because (p. 352) nitrogen tetroxide is decomposed at about 154°, and therefore cannot be formed at 2000°.

Next, the air containing NO_2 is passed through absorbing towers, down which *water* trickles, and nitric acid is formed:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO.$$

The NO liberated combines with more atmospheric oxygen to form NO_2, which interacts again with the water, and practically no nitric oxide is lost.

Finally, the nitric acid is poured upon limestone ($CaCO_3$), and the calcium nitrate formed is sold for use as a fertilizer, under the name **air saltpeter.**

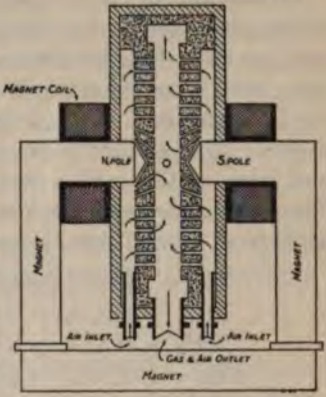


Fig. 96.

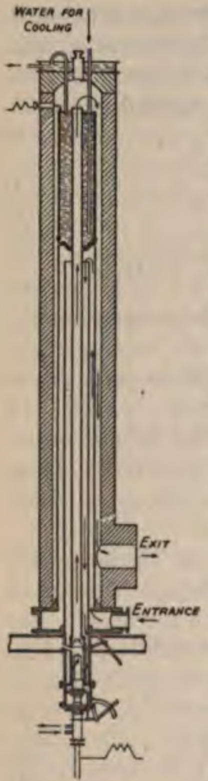


Fig. 97.

The Plant used in the Fixation.—At Notodden and elsewhere in Norway, the **Birkeland-Eyde process** (Fig. 96) is used. Hydroelectric power is employed, and an arc discharge between two rods of carbon is spread, by the influence of large and powerful electromagnets, into a circular brush discharge several feet in diameter. The figure is a cross section of the space filled by the discharge, the small circle in the center being a section of one carbon rod. Air is blown through the flame in such a way that none can avoid passing through at least a part of the heated area. The yield is about 70 g. of nitric acid per kilowatt-hour, and the net earnings are $350,000 (1911).

The **Badische process,** used in the same factories in Norway, employs a discharge through a tube over 20 feet long (Fig. 97). The stream of air rotates as it traverses the tube, so that every part is exposed to the discharge. The **Pauling process,** used at Gelsenkirchen in Germany and Nitrolee, South Carolina, uses preheated air and a different arrangement of the discharge.

For other reactions involving the fixation of atmospheric nitrogen, see calcium cyanamide (*q.v.*) and root nodules (p. 339).

Oxidizing Actions of Nitric Acid

When nitric acid gives up oxygen to any body, it is itself reduced. Hence, according to convenience, we shall refer to oxidations by, or reductions of nitric acid.

Oxidation of Hydrogen. — The metals preceding hydrogen in the electromotive series (p. 260) displace hydrogen from nitric acid, as they do from other acids. With metals more active than zinc, such as magnesium, a great part of the hydrogen escapes in the free condition. But, in the case of zinc and the metals below it, most or all of the hydrogen is oxidized to water by the nitric acid, and part of the acid is reduced (see Active hydrogen, p. 360). Thus, with zinc and *very dilute* nitric acid, almost the only product, aside from zinc nitrate, is ammonia:

$$\begin{array}{lr}
4Zn + 8HNO_3 \rightarrow 4Zn(NO_3)_2(+ 8H). & (1)\\
(8H) + HNO_3 \rightarrow NH_3 + 3H_2O. & (2)\\
NH_3 + HNO_3 \rightarrow NH_4NO_3. & (3)\\
\hline
4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O. &
\end{array}$$

With the excess of nitric acid (3), ammonium nitrate is formed.

Heavy Metals. — The less active metals, such as copper and silver, do not displace hydrogen from dilute acids (p. 60), but reduce nitric acid, nevertheless, and are converted into nitrates. Platinum and gold (*cf.* p. 287) alone are not attacked. Thus, copper, with somewhat *diluted* nitric acid (sp. gr. 1.2), gives cupric nitrate and nitric oxide NO.

In **making the equation** for this action we may use the **anhydride plan** (p. 325), which is applicable whenever an oxygen acid gives an oxide by reduction. We resolve the formula of nitric acid into those of water and the **anhydride** $H_2O,N_2O_5(= 2HNO_3)$. This shows that the two molecules of the acid will give 2NO, and 3O will remain:

$$\begin{array}{lr}
2HNO_3 \text{ (or } H_2O,N_2O_5) \rightarrow H_2O + 2NO\ (+ 3O). & (1)\\
(3O) + 6HNO_3 + 3Cu \rightarrow 3H_2O + 3Cu(NO_3)_2. & (2)\\
\hline
8HNO_3 + 3Cu \rightarrow 4H_2O + 2NO + 3Cu(NO_3)_2. &
\end{array}$$

The nitric oxide is liberated as a colorless gas, but forms the brown tetroxide at once on meeting the oxygen of the air (p. 351).

When *concentrated* nitric acid is used with copper, almost pure nitrogen tetroxide is obtained:

$$
\begin{array}{ll}
2HNO_3\ (\text{or } H_2O,N_2O_5) \rightarrow H_2O + 2NO_2\ (+\ O). & (1) \\
(O) + 2HNO_3 + Cu \rightarrow H_2O + Cu(NO_3)_2. & (2) \\
\hline
4HNO_3 + Cu \rightarrow 2H_2O + 2NO_2 + Cu(NO_3)_2. &
\end{array}
$$

The reader should note the constant production of **nitric oxide with diluted nitric acid,** and the invariable formation of **nitrogen tetroxide with concentrated acid.** This is explained by the fact that nitrogen tetroxide cannot pass unchanged through a liquid containing much water, for it gives nitric acid and nitric oxide with the latter (p. 352). Conversely, where the nitric acid is concentrated, nitric oxide, even if formed by the interaction with the metal, must be oxidized to nitrogen tetroxide as it passes up through the liquid (p. 351). Note, also, that the nitrate of the metal is formed, if the nitrate is not hydrolyzed by water, *not* the oxide.

Oxidation of Non-Metals. — With non-metals the actions are different, in so far that these elements form no nitrates. Thus sulphur boiled in nitric acid gives sulphuric acid, along with nitric oxide, equation (3), or with nitrogen tetroxide, equation (6), or with both, according to the concentration of the acid (see above):

$$
\begin{array}{ll}
2HNO_3\ (\text{or } H_2O,N_2O_5) \rightarrow 2NO + H_2O\ (+\ 3O). & (1) \\
(3O) + H_2O + S \rightarrow H_2SO_4. & (2) \\
\hline
2HNO_3 + S \rightarrow 2NO + H_2SO_4. & (3) \\
2HNO_3\ (\text{or } H_2O,N_2O_5) \rightarrow 2NO_2 + H_2O + O \quad \times 3. & (4) \\
(3O) + H_2O + S \rightarrow H_2SO_4. & (5) \\
\hline
6HNO_3 + S \rightarrow 6NO_2 + 2H_2O + H_2SO_4. & (6)
\end{array}
$$

The reader will note that a separate equation, (3) and (6), must be made for the formation of *each* reduction product. If NO and NO_2 are both formed, they cannot arise from the same molecule of nitric acid. They result from two actions which are independent, although proceeding concurrently in the same vessel (*cf.* p. 317). Thus the equation: $2HNO_3 + C \rightarrow H_2O + CO_2 + NO + NO_2$, is a misrepresentation. It implies that equimolar quantities of the two oxides of nitrogen are formed. But this could occur only by chance, and the balance would be destroyed the next moment by the lowering in the concentration of the acid, giving the advantage to the nitric oxide.

Oxidation of Compounds: Aqua Regia. — Compounds like hydrogen sulphide and sulphurous acid, which are easily oxidized, interact with nitric acid. With diluted nitric acid, the products are free sulphur and sulphuric acid respectively.

The mixture of nitric acid and hydrochloric acid is known as *aqua regia.* Chlorine is set free by the oxidation of the hydrochloric acid,

$$HNO_3 + 3HCl \rightarrow 2H_2O + Cl_2 + NOCl,$$

and nitrosyl chloride NOCl is also formed. The liquid thus contains several oxidizing agents, nitric acid, hypochlorous acid (from $Cl_2 + H_2O$), and some nitrous acid. It is frequently used in analysis, for example to oxidize sulphur (say, in cast iron or in minerals), the sulphuric acid formed being estimated by precipitation and weighing of barium sulphate (p. 287).

Aqua regia (Lat., *royal water*) received its name because it converted the "noble" metals, gold and platinum, into soluble compounds. This it does because the free chlorine, in presence of hydrochloric acid, combines to form the exceedingly stable complex ions (see pp. 505, 508) $AuCl_4^-$ (see chlorauric acid, and $PtCl_6^=$, the negative ion of chloroplatinic acid:

$$2HCl + 2Cl_2 + Pt \rightarrow H_2PtCl_6, \text{ or } Pt + 2Cl_2 + 2Cl^- \rightarrow PtCl_6^=.$$

NITROUS ACID, HYPONITROUS ACID, AND THEIR ANHYDRIDES

Nitrites and Nitrous Acid. — When the nitrates of potassium and sodium are heated, they lose one unit of oxygen, and the **nitrites** remain:

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2.$$

Commonly lead is stirred with the melted nitrate and assists in the removal of the oxygen. The litharge PbO which is formed remains as a residue when the sodium nitrite is dissolved for recrystallization.

When an acid is added to a *dilute* solution of a nitrite, a pale-blue solution containing **nitrous acid** HNO_2 is obtained. The acid is very unstable, however, and, when the solution is warmed, it decomposes:

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O.$$

When a *concentrated* solution of sodium nitrite (or the solid salt itself) is acidified, the nitrous acid decomposes at once, and a brown gas containing the anhydride escapes:

$$2H^+ + 2NO_2^- \leftrightarrows 2HNO_2 \leftrightarrows H_2O + N_2O_3\uparrow.$$

This behavior distinguishes a nitrite from a nitrate.

Nitrous acid is an active oxidizing agent:

$$2HI + 2HNO_2 \text{ (or } H_2O,N_2O_3) \rightarrow 2H_2O + 2NO + I_2.$$

Indigo is also converted by it into isatin (*cf.* p. 311).

Nitrous acid is much used in the making of organic dyes.

Nitrous Anhydride N_2O_3.—A study of the density of the gas arising from the decomposition of nitrous acid shows that, in the gaseous state, the anhydride is almost entirely dissociated:

$$N_2O_3 \rightleftarrows NO + NO_2.$$

When the mixture is led through a U-tube immersed in a freezing mixture at −21°, a deep-blue liquid is obtained which is the anhydride itself. This dissociates rapidly when allowed to boil.

The same equimolar mixture of the two gases is obtained by the action of water on nitrosylsulphuric acid (p. 281).

Hyponitrous Acid and Nitrous Oxide N_2O. — Hyponitrous acid $H_2N_2O_2$ is a white solid. Its solution in water is an exceedingly feeble acid. The warm aqueous solution decomposes slowly, giving nitrous oxide:

$$H_2N_2O_2 \rightarrow H_2O + N_2O,$$

and this change is *not* capable of reversal.

Nitrous oxide is prepared by gently heating ammonium nitrate (an explosive), or a solution of a salt of ammonium and a nitrate:

$$NH_4^+ + NO_3^- \rightleftarrows NH_4NO_3 \rightarrow 2H_2O + N_2O.$$

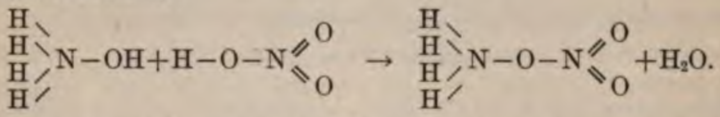
The steam condenses, and the nitrous oxide may be collected over warm water, or be dried and compressed into steel cylinders.

Its solubility in cold water is considerable: at 0°, 130 volumes in 100; at 25°, 60 in 100. The liquefied gas boils at $-89.8°$ and its vapor tension at 20° is 49.4 atmospheres.

A glowing splinter of wood bursts into flame in nitrous oxide, and phosphorus and sulphur burn in it with much the same vigor as in oxygen. In all cases oxides are formed, and nitrogen is set free. It does not combine with nitric oxide, however, as does oxygen (p. 351).

Metals do not rust in nitrous oxide, and the hæmoglobin of the blood is unable to use it as a source of oxygen. It is employed as an anæsthetic for minor operations. The hysterical symptoms which accompany its use caused it to receive the name of "laughing gas."

Graphic Formulæ of Nitric Acid and its Derivatives: Explosives. — The following equation for the formation of ammonium nitrate by neutralization of ammonium hydroxide with nitric acid shows the graphic (p. 292) or structural formulæ of these substances:



$$\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\rangle N-OH+H-O-N\left\langle\begin{matrix}O\\O\end{matrix}\right. \rightarrow \left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\rangle N-O-N\left\langle\begin{matrix}O\\O\end{matrix}\right. +H_2O.$$

The structural formula of the nitrate is intended to explain the fact that the salt is able to exist at all, by representing the oxygen and hydrogen as being separated from one another and attached to different nitrogen units. When the equilibrium of the system is disturbed by heating, the oxygen and hydrogen unite to form water, an arrangement which is much more stable, and nitrous oxide (p. 357) escapes with the steam.

The behavior of nitroglycerine and guncotton (p. 350), as well as of ammonium nitrite (p. 338), is explained in the same way. These substances are made by actions which, like the above neutralization, take place in the cold, and the groups, containing the oxygen on the one hand and carbon and hydrogen on the other, become quietly united without more serious interaction. When, however, the nitroglycerine, for example, is heated, or receives a mechanical shock, the carbon and hydrogen unite with the oxygen and the nitrogen escapes:

$$4C_3H_5(NO_3)_3 \rightarrow 12CO_2 + 10H_2O + 6N_2 + O_2.$$

Smokeless Powder and Dynamite. — Dried guncotton (p. 350) simply burns briskly (deflagrates) when set on fire. Whether wet or dry, it explodes, but only from a suitable shock, such as that produced by fulminate of mercury $Hg(OCN)_2$, used in percussion caps. In pure form it is used only in torpedoes or submarine mines. Like nitroglycerine (p. 350), it explodes too rapidly, and would burst the gun, or pulverize the ore or coal if used for blasting. Neither of these substances "explodes downwards only." The explosion strikes the air with equal violence, but the *effect* on the air escapes notice because it is not permanent, while the shattering of a rock or plate of steel remains.

Cordite, one variety of smokeless powder, is made by dissolving guncotton (65 parts), nitroglycerine (30 parts) and vaseline (5 parts) in acetone. The resulting paste is rolled out and cut into small pieces. When the acetone evaporates, the horny cordite remains. These explosives are *smokeless* because, unlike gunpowder and T.N.T., they yield no solids when they decompose (see equations).

Various forms of dynamite are made like cordite, excepting that sodium or ammonium nitrate and sawdust or flour are added, so that the rate of explosion may be regulated and the coal or ore may be split up, but not shattered or pulverized.

Plastics. — A guncotton, less completely "nitrated" by nitric acid, when worked between rollers with camphor and a little alcohol, gives a viscous solution (Parkes, before 1855). When the alcohol evaporates, transparent, colorless **celluloid** (first made by Hyatt) remains. The moist dough is rolled into sheets to make photographic films. By adding dyes and "fillers," and molding the dough, black combs, brush handles, white knife handles, etc., can be manufactured.

Collodion is a solution of the same guncotton in a mixture of alcohol and ether. When collodion is forced through minute holes in a steel dye, the threads dry as they come out and can be wound on spools. Treatment with an alkali "denitrates" the threads, restoring the composition to that of the original cotton. The product, one of the forms of **artificial silk,** is at least as brilliant as the real article (a protein, not related chemically to cotton), and susceptible of being dyed to any desired tint.

Balancing Equations. — The reader should practice the balancing of the equations for oxidations occurring in this chapter, using all the methods. We have used the anhydride plan (p. 355) and that of partial equations (p. 350). To illustrate the other plans, take the action of concentrated nitric acid on copper (p. 355).

Positive and negative valence method (p. 322). Write the skeleton equation:

Skeleton: $HNO_3 + Cu \rightarrow H_2O + NO_2 + Cu(NO_3)_2.$

We perceive that on the left the valence of O_3 is -6 and of H is $+1$: that of N is therefore $+5$. That of Cu is zero. On the right, the valence of N is $+4$ and of Cu $+2$. Evidently, 2N changing from $2 \times +5$ to $2 \times +4$ will furnish $+2$ for the copper. We note also that $2NO_3$ is required, without change, for $Cu(NO_3)_2$. Hence, altogether $4HNO_3$ is needed on the left, and gives $2NO_2$:

Balanced: $4HNO_3 + Cu \rightarrow 2H_2O + 2NO_2 + Cu(NO_3)_2.$

Positive electrical charge plan (p. 325). In the skeleton equation (above) we first separate the oxidizing ions and their products from the oxidized substance and the change it undergoes:

$$\begin{array}{rcl}
NO_3^- + 2H^+ & \rightarrow & NO_2^0 + H_2O + \oplus \qquad \times 2. \\
Cu^0 + 2\oplus & \rightarrow & Cu^{++}. \\
\hline
Cu^0 + 2NO_3^- + 4H^+ & \rightarrow & 2NO_2^0 + 2H_2O + Cu^{++}.
\end{array}$$

The first partial equation produces $\oplus$, while the second requires $2\oplus$, and hence the former is multiplied by 2 before the addition takes place. Since NO_3^- is the only acid radical present, it is understood that cupric nitrate is the salt formed.

Active ("Nascent") Hydrogen. — When hydrogen gas is led through cold nitric acid, little or no action occurs. But (p. 354) when zinc, which interacts with acids to give hydrogen, is placed in nitric acid the latter is reduced. To explain the apparent greater activity of the hydrogen in the second instance, we note the fact that it is liberated *on the surface of the zinc.* The contact (catalytic) effect of the zinc increases its activity. Many metals have, in a greater or less degree, this power of increasing the activity of hydrogen. Thus, hydrogen absorbed in platinum or palladium (p. 57) or liberated by electrolysis on poles made of these metals, reduces nitric acid readily. Other elements, such as the oxygen used in making sulphur trioxide (p. 279), are also rendered more active by contact agents.

This **more active** state of hydrogen is described as the **nascent state,** because it happens to be a common condition of hydrogen when associated with substances which produce it. The active state has, however, no necessary connection with such an immediately preceding act of liberation, as the platinum and sulphur trioxide illustrations, and the following experiment show: Three test-tubes are filled with dilute, acidified potassium permanganate solution. Zinc dust, added to one, generates hydrogen and causes decolorization. A little platinum black is added to the second, and hydrogen gas is led through this and the third. The contact action of the platinum enables the hydrogen quickly to reduce the permanganate, while the third portion remains unaltered.

Besides, if the action were due to freshly liberated, perhaps atomic hydrogen, this substance should have constant properties. But it has not. Thus, nitric acid with zinc gives much ammonia; with magnesium, none; with tin, ammonia and hydroxylamine $HONH_2$ as well.

Exercises. — 1. Make the equation for the interaction of ferrous chloride, hydrochloric acid, and nitric acid (p. 350), and for all the actions concerned when the test for a nitrate (p. 351) is applied to sodium nitrate. What volume (at 0° and 760 mm.) of NO is obtained from one formula-weight of nitric acid (p. 350)?

2. In the action of zinc on dilute nitric acid (p. 354), why is not the ammonia given off as a gas? How should you show that it was formed at all?

3. Make correct equations for the formation of nitric oxide and nitrogen tetroxide by the action of carbon on nitric acid (p. 355).

4. Make equations for the interaction of iron with diluted and with concentrated nitric acid, respectively (p. 355). The iron gives ferric nitrate $Fe(NO_3)_3$.

5. Give the three ways in which nitrates decompose when heated, with one equation illustrating each.

6. Make all the equations for oxidations on pp. 350 and 354, using the methods illustrated on p. 360.

CHAPTER XXVII

PHOSPHORUS

The Chemical Relations of the Element. — There are many things in the chemistry of phosphorus and its compounds which remind us of nitrogen. Yet these are largely referable to the fact that the elements are both non-metals and both have the same valences, viz., three and five. The behavior of the compounds is often very different. For the present it is sufficient to say that both give compounds with hydrogen, NH_3 and PH_3, and both yield oxides of the forms X_2O_3, X_2O_4, and X_2O_5. The first and last of these oxides are acid-forming, and phosphorus, therefore, gives acids corresponding to nitrous and nitric acids. The element is thus a non-metal.

Occurrence. — This element is found in nature in the form of phosphates. Calcium phosphate $Ca_3(PO_4)_2$ forms 26 per cent of the bones and teeth, and it occurs in all fertile soils. It constitutes a large part of the "phosphate rock" of Georgia, Florida, the Carolinas, Tennessee, and of Algeria and Tunis. A conspicuous mineral related to this substance, apatite, $Ca_5F(PO_4)_3$ and $Ca_5Cl(PO_4)_3$, is found in large quantities in Canada, and is a component of many rocks. Complex organic compounds of phosphorus, such as lecithin, are essential constituents of the muscles, the nerves, and the brain. Amongst foods, egg-yolks and beans contain a large proportion.

Preparation. — Brand, merchant and alchemist, of Hamburg, discovered phosphorus (1669) by distilling the residue from evaporated urine, in the course of his search for the philosopher's stone. The mode of preparing it from **bone-ash**, which contains 83 per cent of calcium phosphate, was first published by Scheele (1771). Now the less expensive calcium phosphate of fossil origin is employed.

The calcium phosphate is mixed with the proper proportions of carbon and silicon dioxide (sand), and the mixture is introduced continuously into an electric furnace (Fig. 98). The discharge of an alternating current between carbon poles produces the very high temperature which the action requires. The calcium silicate which is formed fuses to a slag, and can be withdrawn at intervals. The gaseous products pass off through a pipe and the phosphorus is caught under water:

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 + 5CO + 2P.$$

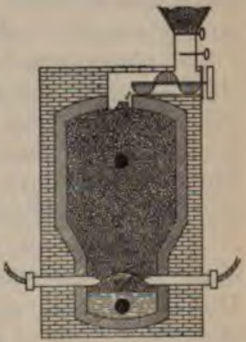


FIG. 98.

We may regard the phosphate as being composed of two oxides, $3CaO,P_2O_5$. It thus appears that the calcium oxide has united with the silica, which is an acid anhydride (*cf.* p. 280): $CaO + SiO_2 \rightarrow CaSiO_3$, while the phosphoric anhydride has been reduced.

The phosphorus, after purification, is cast into sticks in tubes of tin or glass, standing in cold water.

The Electric Furnace. — By an electric furnace is understood an **electrothermal** arrangement in which the heat produced by some resistance offered to the current, such as that of an air-gap between the carbons, is used to produce chemical changes requiring a high temperature. Electrolysis plays no part in the phenomena, and an alternating current, which can produce no electrolytic decomposition, is generally employed. The restricted area within which the heat is developed makes possible the attainment of a high temperature (see Calcium carbide).

Physical Properties. — There are at least two allotropic forms (p. 222) of phosphorus, known as white phosphorus and red phosphorus. **White phosphorus,** prepared as described above, is at first transparent and colorless, but after exposure to light acquires a superficial coating of the red variety. It melts at 44° and boils at 287°. Its sp. gr. is 1.83. Its molecular weight at 313° is 128 and the formula, therefore, P_4 (*cf.* p. 111). Yellow phosphorus is soluble in carbon bisulphide, less soluble in ether, and insoluble in water. It is exceedingly poisonous, less than 0.15 g. being a fatal dose, and is an ingredient in roach-paste and rat poison. Continued exposure to its vapor causes necrosis, a disease from which match-makers are liable to suffer. The jawbones and teeth are particularly liable to attack.

Red phosphorus is a red powder consisting of small tabular crystals. It is obtained by heating yellow phosphorus to about 250° in a vessel from which air is excluded. Much heat is evolved in the transformation. Red phosphorus does not melt, but passes directly into vapor, identical with that of yellow phosphorus. It is insoluble in carbon bisulphide and other solvents. It is not poisonous, and, unlike yellow phosphorus, does not require to be kept under water to avoid spontaneous combustion. Red phosphorus appears to be a solid solution (p. 122) of the white variety in a less active kind. Hence, its properties are variable, *e.g.*, sp. gr. from 2.05 to 2.34. Bridgeman, by heating white phosphorus at 200° under a pressure of 1200 kg./cm^2., has obtained **black phosphorus** (sp. gr. 2.69) which may be the pure form of the red variety.

Chemical Properties. — **White phosphorus** unites directly with the halogens with great vigor. It unites slowly with oxygen in the cold, and with sulphur and many metals when the materials are heated together. The slow union of *cold* phosphorus with atmospheric oxygen is accompanied by the evolution of light. Hence the word phosphorescence. The name of the element (Gk. φῶς, light; φέρω, I bear) records this property. Apparently the chemical energy, transformed in connection with the oxidation, is converted, in part at least, into radiant energy instead of completely into heat.[*] The slow oxidation of phosphorus is accompanied by the production of ozone, but the nature of the action is still unknown (*cf.* p. 219).

Red phosphorus, since it is formed with evolution of heat, contains less energy than white phosphorus and is much less active. It does not catch fire below 240°, while ordinary phosphorus ignites at 35°.

[*] The same production of light from chemical action in a cold body is seen in the luminosity of certain parts of fireflies and some species of fish.

Matches. — In making common matches, invented in 1827, the splints are first dipped in melted sulphur or paraffin to the extent of about half an inch. The head is often composed of lead dioxide PbO_2, which supplies oxygen, a small proportion of free phosphorus or a sulphide of phosphorus P_4S_3 which is readily ignited by friction, and dextrin or glue. The use of white phosphorus is forbidden by law in Sweden, France, Great Britain and Switzerland, and is prevented by a tax of two cents per 100 matches in the United States.

In the case of "safety" matches, the mixture upon the head is not easily ignited by itself. It is composed of potassium chlorate or dichromate, some sulphur or antimony trisulphide Sb_2S_3 (combustible), and a little powdered glass or chalk to increase the friction, all held together with glue. Upon the rubbing surface on the box is a thin layer of antimony trisulphide mixed with red phosphorus, chalk or glass, and glue. The friction converts a little of the red phosphorus into vapor, which catches fire readily.

Phosphine. — Three hydrides of phosphorus are known. These are, phosphine PH_3 (a gas), a liquid hydride P_2H_4, which is presumably the analogue of hydrazine (N_2H_4), and a solid hydride P_4H_2.

Phosphine PH_3 is formed slowly by the action of active hydrogen, from zinc and hydrochloric acid at 70°, upon white phosphorus. The gas may be made by boiling white phosphorus with potassium hydroxide solution in a flask provided with a delivery tube. Potassium hypophosphite is formed at the same time:

$$3KOH + 4P + 3H_2O \rightarrow 3KH_2PO_2 + PH_3\uparrow.$$

The gas made in this way contains a little of the vapor of the liquid hydride, which is spontaneously inflammable, and consequently the bubbles of the mixture catch fire when they reach the surface of water in the trough: $PH_3 + 2O_2 \rightarrow H_3PO_4$. In still, moist air, the fog of droplets of phosphoric acid solution form smoke rings.

The simplest method of preparing phosphine is by the action of water upon calcium phosphide:

$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3.$$

This action is analogous to that of water upon magnesium nitride (p. 339), by which ammonia is produced. In consequence of the fact that calcium phosphide is a substance of irregular composition, a mixture of all three hydrides is generally obtained. By passing the gas through a strongly cooled delivery tube, however, the liquid and solid compounds are condensed and fairly pure phosphine passes on.

Phosphine is a colorless gas, which is easily decomposed by heat into its elements. It is exceedingly poisonous and, unlike ammonia, it is insoluble in water, and produces no basic compound corresponding to ammonium hydroxide when brought in contact with this substance. It resembles ammonia, formally at least, in uniting with the hydrogen halides (see below). It differs from ammonia, however, inasmuch as it does not unite with the oxygen acids. Phosphine acts upon solutions of some salts, precipitating phosphides of the metals:

$$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2\downarrow + 3H_2SO_4.$$

Phosphonium Compounds. — Hydrogen iodide unites with phosphine to form a colorless solid, crystallizing in beautiful, highly refracting, square prisms: $PH_3 + HI \rightarrow PH_4I$. Hydrogen chloride combines similarly with phosphine, but only when the gases are cooled by a freezing mixture, or are brought together under a total pressure of 18 atmospheres at 14°. When the pressure is released, rapid dissociation occurs.

In imitation of the ammonia nomenclature, these substances are called **phosphonium iodide** and phosphonium chloride PH_4Cl. They are entirely different, however, from the corresponding ammonium derivatives, for the PH_4^+ ion is unstable. When brought in contact with water they decompose into their constituents, the hydrogen halide going into solution, and the phosphine being liberated as a gas.

Halides of Phosphorus. — The existence of the following halides has been proved conclusively:

. . . .	. . . . .	. . . . .	P_2I_4 (solid)
PF_3 (gas)	PCl_3 (liquid)	PBr_3 (liquid)	PI_3 (solid)
PF_5 (gas)	PCl_5 (solid)	PBr_5 (solid)	. . . . .

These substances may all be formed by direct union of the elements. They are incomparably more stable than are the similar compounds of nitrogen. They are all hydrolyzed by water, and give an oxygen acid of phosphorus and the hydrogen halide (see below). This action was used in the preparation of hydrogen bromide (p. 197) and hydrogen iodide (p. 201).

Phosphorus trichloride PCl_3 is made by passing chlorine gas over melted phosphorus in a flask until the proper gain in weight has occurred. The substance, which is a liquid boiling at 76°, is stable (*cf.* p. 93). When excess of chlorine is employed, **phosphorus pentachloride** PCl_5, which is a white solid body, is formed. When moist air is blown over any of these substances, the water is condensed to a fog by the hydrogen halide. In the case of the interaction of phosphorus pentachloride and water, phosphoric acid is formed:

$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl.$$

Phosphorus pentachloride, when heated, reaches a vapor tension of 760 mm. at 163°, and while still solid. At higher pressure it melts at 166°. At these temperatures, about 4 per cent of the molecules are dissociated into phosphorus trichloride and chlorine (p. 117): $PCl_5 \rightleftarrows PCl_3 + Cl_2$.

Oxides of Phosphorus. — The oxides of phosphorus are the so-called trioxide P_4O_6, the pentoxide P_2O_5, and a tetroxide P_2O_4.

The **pentoxide** is a white powder formed when phosphorus is burned with a free supply of oxygen. It unites with water with great violence to form metaphosphoric acid (see below), and hence is known as **phosphoric anhydride**: $P_2O_5 + H_2O \rightarrow 2HPO_3$. In the laboratory this action is frequently utilized for drying gases (p. 330) and for removing water from combination (p. 349). The vapor density leads to the formula P_4O_{10}, use of which, however, would only complicate our equations.

The **trioxide** P_4O_6 is obtained by burning phosphorus in a tube with a restricted supply of air. It is a white solid, melting at 22.5° and boiling at 173°. This oxide is the anhydride of phosphorous acid, but it unites exceedingly slowly with cold water to form this substance. It interacts vigorously with hot water, but phosphine, red phosphorus, hypophosphoric acid, and phosphoric acid are amongst the products, and very little phosphorous acid escapes decomposition. When this oxide is heated to 440° it decomposes, giving the **tetroxide** P_2O_4 and red phosphorus.

Acids of Phosphorus. — There are six different acids of phosphorus. Three are phosphoric acids, representing the same stage of oxidation of phosphorus, but different degrees of hydration of the anhydride. The others show three different and lower states of oxidation (study by positive and negative valences, p. 323):

Orthophosphoric acid	H_3PO_4 (= $3H_2O,P_2O_5$)
Pyrophosphoric acid	$H_4P_2O_7$ (= $2H_2O,P_2O_5$)
Metaphosphoric acid	HPO_3 (= H_2O,P_2O_5)
Hypophosphoric acid	H_2PO_3 (= $2H_2O,P_2O_4$)
Phosphorous acid	H_3PO_3 (= $3H_2O,P_2O_3$)
Hypophosphorous acid	H_3PO_2 (= $3H_2O,P_2O$)

The Phosphoric Acids. — The relation between the three different phosphoric acids may be seen by considering them as being formed from phosphorus pentoxide (the anhydride) and water. In the majority of cases already considered this sort of action takes place in but one way. Thus, nitric acid is known in but one form, which is produced by the union of one molecule each of nitrogen pentoxide and water: $N_2O_5 + H_2O \rightarrow 2HNO_3$. Similarly, the chief sulphuric acid is the one formed from one molecule of sulphur trioxide and one molecule of water: $SO_3 + H_2O \rightarrow H_2SO_4$, although here we have also disulphuric acid $H_2S_2O_7$, or $H_2O,2SO_3$.

Now, when phosphoric anhydride acts upon water we obtain a solution which, on immediate evaporation, leaves a glassy solid, HPO_3, known as **metaphosphoric acid.** This is H_2O,P_2O_5. When, however, the solution is allowed to stand for some days, or is boiled with a little dilute nitric acid, whose hydrogen-ion acts catalytically, the residue from evaporation is H_3PO_4, **orthophosphoric acid:**

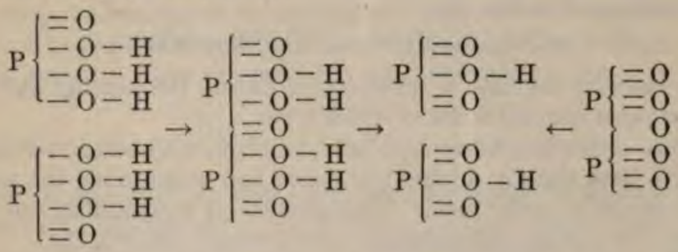
$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4 \quad \text{or} \quad HPO_3 + H_2O \rightarrow H_3PO_4.$$

This acid is $3H_2O,P_2O_5$, and no further addition of water to form a different acid (see p. 370) can be effected.

Conversely, when orthophosphoric acid is kept at about 255° for a time, it slowly loses water, and $H_4P_2O_7$, **pyrophosphoric acid,** is obtained:

$$2H_3PO_4 \rightarrow H_2O + H_4P_2O_7.$$

This acid is $2H_2O,P_2O_5$. Further desiccation leaves metaphosphoric acid, which cannot be further resolved into phosphorus pentoxide and water. When dissolved in water, pyrophosphoric acid slowly resumes the water which it has lost and gives the ortho-acid again. The relations of all these substances are more clearly seen in the graphic formulæ:



$$\begin{array}{c} P\left\{\begin{array}{l} =O \\ -O-H \\ -O-H \\ -O-H \end{array}\right. \\ \\ P\left\{\begin{array}{l} -O-H \\ -O-H \\ -O-H \\ =O \end{array}\right. \end{array} \rightarrow \begin{array}{c} P\left\{\begin{array}{l} =O \\ -O-H \\ -O-H \end{array}\right. \\ =O \\ P\left\{\begin{array}{l} -O-H \\ -O-H \\ =O \end{array}\right. \end{array} \rightarrow \begin{array}{c} P\left\{\begin{array}{l} =O \\ -O-H \\ =O \end{array}\right. \\ \\ P\left\{\begin{array}{l} =O \\ -O-H \\ =O \end{array}\right. \end{array} \leftarrow \begin{array}{c} P\left\{\begin{array}{l} =O \\ =O \end{array}\right. \\ O \\ P\left\{\begin{array}{l} =O \\ =O \end{array}\right. \end{array}$$

A most important fact to be noted is that the *addition or removal of water leaves the valence of the phosphorus unchanged.* The degree of oxidation of the phosphorus and its valence are *identical* in the three acids.

The Relations of Anhydrides and Oxygen Acids. — Considering the anhydride from which an acid is derived gives us the key to the nature and behavior of the acid. It tells much that the formula of the acid does not tell. For example: (1) What is the valence of phosphorus in H_3PO_3? The only way to answer this question is to resolve the formula (doubled, if necessary) into water and the anhydride, $3H_2O,P_2O_3$. The phosphorus is trivalent. (2) How is this acid related to metaphosphoric acid HPO_3? Resolve the latter, as before, H_2O,P_2O_5. The answer is that in the latter the phosphorus is quinquivalent. (3) How can we get phosphorous acid from metaphosphoric acid, or *vice versa?* Considering the anhydrides, we answer, by reduction and oxidation, respectively. (4) Is pyrophosphoric acid $H_4P_2O_7$, because it contains 7O, to be made from all others by oxidation? Resolve it into water and anhydride, $2H_2O,P_2O_5$. We then perceive that to make it from phosphorous acid requires oxidation, but to make it from ortho- or metaphosphoric acid requires only a change in the degree of hydration: *adding or subtracting water*, since it adds or subtracts hydrogen and oxygen in equivalent amounts, *is not* *oxidation or reduction.* These conceptions have been discussed before (pp. 316, 321).

Orthophosphoric Acid H_3PO_4.—The impure, commercial acid is made by mixing selected, pulverized phosphate rock $Ca_3(PO_4)_2$ with sulphuric acid (sp. gr. 1.5) and heating with steam and stirring in a wooden vat.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \leftrightarrows 2H_3PO_4 + 3CaSO_4\downarrow.$$

The calcium sulphate is precipitated during the heating and the subsequent concentration of the filtrate.

Pure orthophosphoric acid may be made by boiling red phosphorus with slightly diluted nitric acid and evaporating the water and excess of nitric acid. The product of recrystallization is a white, crystalline, deliquescent, solid hydrate, $2H_3PO_4,H_2O$.

The acid is **much weaker** than sulphuric acid, and is dissociated chiefly into the ions H^+ and $H_2PO_4^-$. The dihydrophosphate-ion $H_2PO_4^-$, being an acid as well as an ion, is further broken up to some extent into H^+ and $HPO_4^=$, as we learn from the fact that the solution of the sodium salt NaH_2PO_4 is acid. The ion $HPO_4^=$ is hardly dissociated at all, for a solution of the salt Na_2HPO_4 is not acid in reaction.

Salts of Orthophosphoric Acid. — As a **tribasic acid,** it forms salts of three kinds, such as NaH_2PO_4, Na_2HPO_4, and Na_3PO_4. These are known respectively as **primary, secondary,** and **tertiary** sodium orthophosphate. The primary sodium phosphate is faintly acid in reaction. The secondary one is slightly alkaline, because of hydrolysis arising from the tendency of the hydrogen-ion of the water to combine with the $HPO_4^=$ to form $H_2PO_4^-$, which is much more feebly acid than is phosphoric acid H_3PO_4. The simplified equation (p. 271) shows the reason for the alkalinity of the solution: $HPO_4^= + H^+ + OH^- \rightarrow H_2PO_4^- + OH^-$, for hydroxyl-ion is present. The tertiary phosphate is stable only in solid form, and can be made by evaporating to dryness a mixture of the secondary phosphate and sodium hydroxide:

$$Na_2HPO_4 + NaOH \rightleftarrows Na_3PO_4 + H_2O\uparrow.$$

When the product is dissolved in water, this action is reversed (*cf.* p. 271). Mixed phosphates are also known, particularly sodium-ammonium phosphate (**microcosmic salt**) $NaNH_4HPO_4,4H_2O$, and the insoluble magnesium-ammonium phosphate $MgNH_4PO_4$. Primary calcium phosphate (*q.v.*), known in commerce as "superphosphate," is used as a fertilizer.

The tertiary **phosphates** are unchanged by **heating.** The primary and secondary phosphates, however, retaining, as they do, some of the original hydrogen of the phosphoric acid, are capable of losing water, like phosphoric acid itself, when heated. The actions are slowly reversed when the products are dissolved in water:

$$NaH_2PO_4 \rightleftarrows NaPO_3 + H_2O\uparrow.$$
$$2Na_2HPO_4 \rightleftarrows Na_4P_2O_7 + H_2O\uparrow.$$

It will be seen that the **meta-** and **pyrophosphates of sodium** are formed by these actions; and this is indeed the simplest way of forming these substances, since the acids themselves are not permanent in solution, and are too feeble to lend themselves to exact neutralization. Ammonium salts of phosphoric acid lose ammonia, as well as water, when heated (*cf.* p. 344, last par.). Thus, microcosmic salt gives primary sodium phosphate:

$$NaNH_4HPO_4 \rightarrow NH_3\uparrow + NaH_2PO_4 \rightarrow NaPO_3 + H_2O\uparrow,$$

and this in turn is converted into the metaphosphate by loss of water.

Pyrophosphoric Acid and Metaphosphoric Acid. — **Pyrophosphoric acid** $H_4P_2O_7$, although tetrabasic, gives only the neutral salts, such as $Na_4P_2O_7$, and those in which one-half of the hydrogen has been displaced by a metal, such as $Na_2H_2P_2O_7$.

Metaphosphoric acid HPO_3 is the "glacial phosphoric acid" of commerce, and is usually sold in the form of transparent sticks. It is obtained by heating orthophosphoric acid, or by direct union of phosphorus pentoxide with a small amount of cold water. It passes into vapor at a high temperature, and its vapor density corresponds to the formula $(HPO_3)_2$.

Sodium metaphosphate $NaPO_3$, in the form of a small globule obtained by heating microcosmic salt on a platinum wire, is used in analysis. When minute traces of oxides of certain metals are placed upon such a globule, known as a **bead,** and heated in the Bunsen flame, the mass is colored in various tints according to the oxide used (**bead test**). This action may be understood when we consider that sodium metaphosphate takes up water to form primary sodium orthophosphate: $NaPO_3 + H_2O \rightarrow NaH_2PO_4$. In the same way, but at higher temperatures, it is able to take up oxides of elements other than hydrogen, giving mixed orthophosphates. Thus, with oxide of cobalt a part of the metaphosphate unites according to the equation:

$$NaPO_3 + CoO \rightarrow NaCoPO_4,$$

and the product gives a blue color to the bead.

Distinguishing Tests. — When a solution of **nitrate of silver** is added to a solution of orthophosphoric acid, or to any soluble orthophosphate, a yellow precipitate of silver orthophosphate Ag_3PO_4 is produced. This is a test for orthophosphate-ion. With pyrophosphoric acid or any pyrophosphate the product is white $Ag_4P_2O_7$. With metaphosphoric acid a white precipitate, $AgPO_3$, is obtained also. Metaphosphoric acid coagulates a clear solution (colloidal suspension) of albumin (say, white of egg), while ortho- or pyrophosphoric acid has no visible effect upon it (p. 417).

Phosphorous Acid H_3PO_3. — When added to cold water, phosphorus trioxide (P_4O_6) yields phosphorous acid very slowly. With hot water the action is exceedingly violent and complex (p. 367). This acid may be obtained easily by the action of water upon phosphorus trichloride, tribromide (p. 197), or tri-iodide and evaporation of the solution:

$$PCl_3 + 3H_2O \rightarrow P(OH)_3 + 3HCl\uparrow.$$

Some of this acid, along with phosphoric acid and hypophosphoric acid, is formed when moist phosphorus oxidizes in the air.

In spite of the presence of three hydrogen atoms, this acid is dibasic, and two only are replaceable by metals. To express this fact, the first of the following formulæ is preferred:

$$O = P\left\{\begin{array}{l} -H \\ -O-H \\ -O-H \end{array}\right. \qquad\qquad P\left\{\begin{array}{l} -O-H \\ -O-H \\ -O-H \end{array}\right.$$

since the symmetrical formula would indicate no difference between the three hydrogen atoms. H united directly to P, as here and in PH_3, is not acidic. Phosphorous acid is a powerful reducing agent, precipitating silver, for example, in the metallic form from solutions of its salts. When heated, it decomposes, giving the most stable acid of phosphorus (*cf.* pp. 290, 308, 314, 320, 357), namely, metaphosphoric acid, and phosphine:

$$4H_3PO_3 \rightarrow 3HPO_3 + 3H_2O + PH_3.$$

Sulphides of Phosphorus. — White phosphorus, when heated with sulphur, unites with explosive violence. By using red phosphorus the action can be controlled. By employing the proper proportions the **pentasulphide** P_2S_5 is secured. It is purified by distillation, and is a yellow crystalline solid (m.-p. 274°, b.-p. 530°). Phosphorus pentasulphide is hydrolyzed by cold water:

$$P_2S_5 + 8H_2O \rightarrow 2H_3PO_4 + 5H_2S.$$

Other sulphides, P_4S_3 (used in making matches), P_2S_3, and P_3S_6, may be prepared by using the constituents in the proportions represented by these formulæ.

Comparison of Phosphorus with Nitrogen and with Sulphur. — Although phosphorus and nitrogen are regarded as belonging to one family, the differences between them are more conspicuous than the resemblances. The latter are confined almost wholly to matters concerned with valence. The differences are seen in the facts that nitrogen is a gas and exists in but one form, while phosphorus is a solid occurring in two varieties, and that the former is inactive and the latter active. The contrasts between phosphine and ammonia (p. 366) and between the halides of the two elements (pp. 346, 367) have been noted already. The pentoxide of nitrogen decomposes spontaneously; that of phosphorus is one of the most stable of compounds. Nitric acid is very active, both as acid and oxidizing agent; the phosphoric acids are quite the reverse.

On the other hand, the resemblance of phosphorus to sulphur is marked. Both are solids, existing in several forms. Both yield stable compounds with oxygen and chlorine. The hydrogen compounds interact with salts to give phosphides of metals and sulphides of metals, respectively. Against these must be set the facts, that hydrogen sulphide does not unite with the hydrogen halides at all while phosphine gives the phosphonium halides, and that phosphoric acid is hard to reduce while sulphuric acid is reduced with comparative ease.

Exercises. — 1. What are the valences of the non-metals in: $H_2S_2O_7$, $H_2Cr_2O_7$, $KMnO_4$, KH_2PO_2, H_3NO_4, NaH_2PO_3, Na_2PO_3? Name these substances.

2. Is it oxidation or reduction, or neither, when we make, (*a*) N_2O_4 from HNO_3, (*b*) SO_2 from H_2SO_3, (*c*) HPO_3 from H_3PO_3, (*d*) $H_2S_2O_7$ from H_2SO_4, (*e*) Na_2SO_4 from $NaHSO_3$?

3. Why would a mixture of potassium dichromate and hydrochloric acid (p. 270) be less suitable than nitric acid, as an oxidizing agent for making phosphoric acid from red phosphorus?

4. Why is not the tertiary phosphate of sodium (p. 371) decomposed by heating? What tertiary phosphates would be decomposed by this means?

5. Formulate the hydrolyses of the secondary and tertiary sodium orthophosphates as was done for sodium sulphide (p. 271).

6. How should you prepare $Ca_2P_2O_7$ and $Ca(PO_3)_2$, both insoluble?

7. What product should you confidently expect to find after heating (p. 371), (*a*) sodium phosphite, Na_2HPO_3, (*b*) potassium hypophosphite? Make the equations.

8. Compare the elements chlorine and phosphorus after the manner of the comparisons on p. 373.

CHAPTER XXVIII

CARBON AND THE OXIDES OF CARBON

THE majority of the substances composing, or produced by, living organisms, such as starch, fat, and sugar, are compounds of carbon. Hence the chemistry of these compounds is known as organic chemistry. It was at first supposed that the artificial production of such compounds, *e.g.*, without the intervention of life, was impossible. But many natural organic products have now been made from simpler ones or from the elements, and the preparation of the others is delayed only in consequence of difficulties caused by their instability and complexity. On the other hand, hundreds of compounds unknown to animal or vegetable life, including many valuable drugs and dyes, have now been added to the catalogue of chemical compounds. More than 200,000 different compounds containing carbon are known, and thousands are added every year.

The elements entering into carbon compounds are chiefly hydrogen and oxygen. After these, nitrogen, phosphorus, the halogens and sulphur may be named.

CARBON C

Occurrence. — Large quantities of carbon are found in the free condition in nature. The diamond is the purest natural carbon. Graphite, or plumbago, which is the next purest, is found in limited amounts, and is a valuable mineral. Coal occurs in numerous forms containing greatly varying proportions of free carbon. Small quantities of the free element have been found in meteorites.

In combination, carbon is found in marsh-gas, or methane CH_4, which is the chief component of natural gas. The numerous compounds found in plants and animals have already been mentioned. The mineral oils consist almost entirely of mixtures of various compounds of carbon and hydrogen. Whole geological formations are composed of carbonates of common metals, particularly calcium carbonate or limestone.

Allotropic Forms of Carbon. — The allotropic (p. 222) forms of carbon differ very strikingly in their physical properties. The **diamond** is transparent, crystalline, and very hard (sp. gr. 3.5). **Graphite** is black, lustrous, and very soft (sp. gr. 2.3). **Amorphous carbon** is very variable. Thus lampblack (see p. 398) is a fine powder of nearly pure carbon, charcoal (see p. 408) shows the structure of the wood, and coal (see p. 409) contains compounds of carbon as well as the free element. These amorphous forms can best be discussed after the materials from which they are formed have been considered.

That all the forms are composed of the same element is shown by the fact that they *all* burn in oxygen to give carbon dioxide. Then, too, when heated strongly in absence of air, diamond and the amorphous forms all turn into graphite. They contain different amounts of chemical energy, however. Thus, when 1 g. of each is burned, diamond gives 7805 cal., graphite 7850 and sugar charcoal (p. 286) 8040. The tendency of most carbon compounds, when heated, to **char**, giving free carbon, is used as a **test**.

The Diamond. — Diamonds are found chiefly in Brazil, and South Africa. They are separated by weathering the rock, which then crumbles, and by washing the débris with water. They are covered with a crust which entirely obscures their luster, and possess natural crystalline forms belonging to the regular system, such as the octahedron (p. 83). It should be noted that this natural form bears no relation whatever to the pseudo-crystalline shape which is conferred upon the stone by the diamond-cutter. The natural stone is "cut," by grinding new faces. Thus, a "brilliant" possesses one rather large, flat face, which forms the base of a many sided pyramid (Fig. 99, showing two views). This form is given to the stone, in order that the maximum reflection of light from its interior may be produced. The diamond is harder

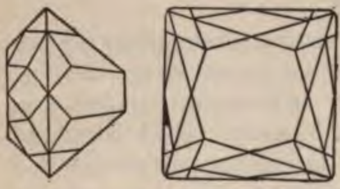


FIG. 99.

(Appendix II) than any other variety of matter, so that it can be scratched or polished only by rubbing with diamond powder. It is the densest form of carbon (sp. gr. 3.5). The colorless stones, and occasional specimens with special tints (like the blue, Hope diamond) are the most valuable. The black ("carbonado") and discolored specimens are used for grinding and glass cutting. Mounted round the edge of a tube, they are used for drilling rock, so that a cylindrical specimen of the whole of the strata can be secured for examination. The forms of carbon are insoluble in all liquids at room temperature. Molten iron (*q.v.*) dissolves five or six per cent, part of which goes into combination; but usually only graphite is found in the cooled product. Moissan (1887), however, succeeded in preparing microscopic fragments of diamonds in this way. The diamond is a nonconductor of electricity.

Diamonds are sold by the new international carat, 200 mgms. (old carat, 4 grains = 205 mgms.), and the value increases with the size. Thus, a first quality, cut stone of 1 carat is worth about $270, one of 2 carats about $340 per carat. The largest diamond known, the *Cullinan* (1905), weighed 3032 (old) carats (621 g. or 1.37 lbs). It was presented by the Transvaal government to King Edward VII, and was cut into stones of 516.5 and 309 carats and many smaller ones. Other large stones are the *Jubilee* (239 carats), and the *Kohinoor* (106 carats).

Graphite. — Graphite (Gk., *I write*) is found in Cumberland, Siberia, Canada, and Ceylon. It is composed of glittering, slippery, crystalline scales (hexagonal system). In utter contrast to the diamond, the mineral is extremely soft, has a smaller specific gravity (2.3), and conducts electricity. It is **made artificially** by an electrothermal process (*cf.* p. 363). A powerful alternating current is passed through a mass of granular anthracite, mixed with pitch and a little sand (Acheson's process). The mixture (3 tons) is piled between the electrodes (Fig. 100) and, on account of its high resistance, becomes strongly heated. The change occupies 24–30 hours.

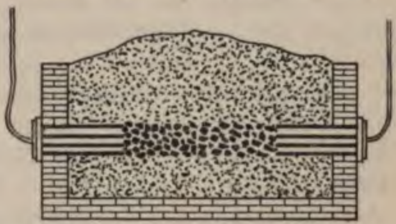


FIG. 100.

Graphite is now used exclusively for making the anodes in the electrolytic manufacture of chlorine and in related processes. Mixed with fine clay it forms the "lead" of lead pencils, first used in the sixteenth century.* Mixed with clay it is used also for making crucibles, which withstand high temperatures and serve for melting and casting steel and high melting alloys. As "black-lead" it forms stove polish, the layer of fine scales protecting the iron against rusting. It is employed as a lubricant in cases where oil would be decomposed by the heat and where wooden surfaces are in contact.

Chemical Properties of Carbon. — The most common uses of carbon depend upon its great tendency to **unite with oxygen,** forming carbon dioxide CO_2. Under some circumstances carbon monoxide CO (see below) is produced. Aside from the direct employment of this action for the sake of the heat which is liberated, it is used also in the **reduction** of ores of iron, copper, zinc, and many other metals. When, for example, finely powdered cupric oxide and carbon are heated, copper is obtained. The gas given off is either carbon dioxide, or a mixture of this with carbon monoxide, according to the proportion of carbon used:

$$CuO + C \rightarrow Cu + CO,$$
$$2CuO + C \rightarrow 2Cu + CO_2.$$

At the high temperatures produced in the electric furnace, carbon **unites with** many **metals** and some **non-metals.** Compounds formed in this way are known as **carbides,** such as aluminium carbide Al_4C_3, calcium carbide CaC_2, and carborundum CSi (see below).

The **union with hydrogen** is ordinarily too slow to be observed. But when the carbon is mixed with pulverized nickel (contact agent), and hydrogen is passed over the mixture at 250°, methane CH_4 is formed (99 per cent). The action is reversible and exothermal, and is therefore, at higher temperature, less complete (*cf.* p. 189), at 850° reaching only 1.5 per cent. On the other hand, an electric arc, between carbon poles in an atmosphere of hydrogen, gives traces of acetylene C_2H_2, this action being endothermal. The other compounds of carbon and hydrogen are all obtained by indirect reactions.

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* Priestley was the first to suggest the use of caoutchouc (raw rubber) as an eraser.

Carbon Disulphide CS_2. — This compound is made by direct union of sulphur vapor and glowing charcoal. An electric furnace like that in Fig. 98 (p. 363) is employed. The substance comes off as a vapor and is condensed.

Carbon disulphide is a colorless, highly refracting liquid (b.-p. 46°). Traces of other compounds give the commercial article a disagreeable smell. It burns in air, forming carbon dioxide and sulphur dioxide. It is an important solvent for sulphur and caoutchouc (rubber), and dissolves iodine and phosphorus freely. Large quantities are employed also in the destruction of prairie dogs and ants and for freeing grain elevators of rats and mice.

Carbon Tetrachloride CCl_4. — This compound is manufactured by leading dry chlorine into carbon disulphide containing a little iodine (contact agent) in solution:

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2.$$

The carbon tetrachloride (b.-p. 77°) is first distilled off, and the sulphur monochloride (b.-p. 136°) is purified for use in vulcanizing rubber.

Carbon tetrachloride is a colorless liquid which dissolves fats, tars, and many other organic compounds. It is used to take the oil or grease out of wool, linen, oil-bearing seeds and bones. It has the advantage over gasoline (petrol) and benzine (see p. 391), which can be used for similar purposes, that it is non-inflammable. "Carbona," used for removing stains from clothing, gloves and shoes, is benzine to which sufficient carbon tetrachloride has been added to render the mixture noninflammable. "Pyrene" fire extinguishers contain, mainly, carbon tetrachloride. The temperature of the burning material is lowered, because heat is consumed in vaporizing the liquid, and, at the same time, the vapor displaces the air and stops the combustion.

Calcium Carbide CaC_2 and Carborundum SiC. — Calcium carbide is manufactured in an electric furnace, by the interaction of finely pulverized limestone or quicklime with coke:

$$CaO + 3C \rightarrow CaC_2 + CO.$$

The operation is a continuous one, the materials being thrown into the left side of the drum (Fig. 101, diagrammatic), and the product removed on the right. The carbon poles are fixed. The arc having been established, the drum is rotated slowly as the carbide accumulates. The current enters by one carbon, passes through the carbide, and leaves by the other. The high resistance of the partially transformed material causes the production of the heat. When the action in one layer approaches completion, the resistance falls, the current increases, and an armature round which the wire passes (not shown in Fig. 101) comes into operation and turns the drum. In this way the carbide just formed is continuously moved away from the carbons, and new material, introduced on the left, falls into the path of the current. The iron plates which form the circumference of the drum are added on the left and removed on the right, where also the carbide is broken out with a chisel. The drum revolves once in about three days. The product is used for making acetylene (*q.v.*).

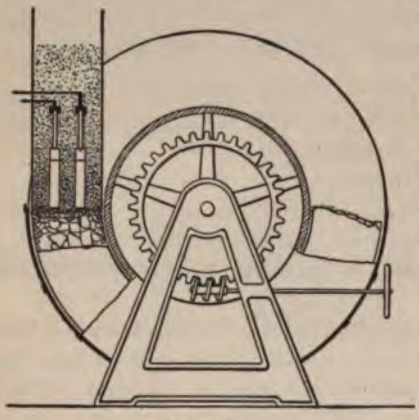


Fig. 101.

Carborundum, or carbide of silicon SiC, of which hundreds of tons are manufactured annually at Niagara Falls (Acheson's process), is made in an electric furnace of the type shown in Fig. 100 (p. 377). A mixture of coke and sand (silicon dioxide SiO_2) with some sawdust is piled between the terminals, with a core of granular carbon to carry most of the current. The resistance produces a high temperature (1950°), and carbon replaces the oxygen:

$$3C + SiO_2 \rightarrow SiC + 2CO.$$

The carborundum remains, often in beautifully crystalline form. It is exceedingly hard (Appendix II), and after pulverization and mixing with a filler, is moulded into grinding wheels.

CARBON DIOXIDE AND CARBONIC ACID

rrence. — Carbon dioxide is present in the atmosphere, ues from the ground in large quantities in certain neighborus, for example, in the so-called Valley of Death in Java, n the Grotta del Cane near Naples. Effervescent mineral rs, such as those of Vichy and of the Geyser Spring at Sara-, contain it in solution, and their effervescence is caused by the pe of the gas when the pressure is reduced.

Modes of Formation. — 1. Carbon dioxide is produced by ombustion of carbon with an *excess* of oxygen: $C + O_2 \rightarrow CO_2$. The combustion of all compounds of carbon, as well as the slow oxidation in the tissues of plants and animals, yield the same product. The product from burning carbon is naturally mixed with at least four times its volume of atmospheric nitrogen. To secure carbon dioxide for commercial purposes from this source, the gas is led under pressure into a solution of potassium carbonate, which absorbs the carbon dioxide:

$$CO_2\,(\text{gas}) \rightleftarrows CO_2\,(\text{dslvd}) + H_2O \rightleftarrows H_2CO_3 + K_2CO_3 \rightleftarrows 2KHCO_3.$$

When the pressure is reduced by a pump, all the actions are reversed, and the gas escapes in pure form. The same solution, with occasional purification, can be used an indefinite number of times.

2. It was Joseph Black (1757) who first recognized the gas as a distinct substance. He observed its formation when marble or magnesium carbonate was heated:

$$CaCO_3 \rightleftarrows CaO + CO_2,$$

and named the gas "fixed air" from the fact that it was contained in these solids. The above action had been used for centuries in making quicklime (calcium oxide). All common carbonates, excepting the normal carbonates of potassium and sodium, decompose, leaving the oxide of the metal or the metal (p. 60).

3. Black found that the gas was also produced when acids acted upon carbonates, and this is the method employed in the laboratory:

$$\left.\begin{array}{r} CaCO_3\,(\text{solid}) \leftrightarrows CaCO_3\,(\text{dslvd}) \leftrightarrows Ca^{++} + CO_3^{=} \\ 2HCl\,(\text{dslvd}) \leftrightarrows 2Cl^{-} + 2H^{+} \end{array}\right\} \leftrightarrows H_2CO_3 \leftrightarrows H_2O + CO_2.$$

Since the carbonic acid is very slightly ionized, the action is like that of acids on sulphites (p. 275). Since, however, the carbonate of calcium (marble) is very slightly soluble, so that an additional equilibrium controls its solution, the action is like that of acids on ferrous sulphide (p. 272). The apparatus shown in Fig. 24 is used. Carbon dioxide is formed in decay (p. 36) and, as Black likewise discovered, in fermentation (*q.v.*).

Physical Properties. — Carbon dioxide is a colorless, odorless gas. It is heavier than air. The G.M.V. weighs 44.26 g. Its critical temperature is 31.35° (p. 79). The solid melts at −56°, having a vapor pressure of 5.3 atmospheres. The solid has a vapor pressure of 1 atmos. at −79°. The sp. gr. of the liquid at 0° is 0.95. At 0° its vapor tension is 35.4 atmospheres and at 20°, 59 atmospheres. It must be preserved, therefore, in very strong cylinders of mild steel. Large quantities of it, often collected from fermentation vats, are sold in such cylinders, and used in operating beer-pumps and in making aerated waters. When the liquid is allowed to flow out into an open vessel or, still better, into a cloth bag (non-conductor of heat), it cools itself by its own evaporation and forms a white, snowlike mass. Solid carbon dioxide evaporates at −79°, without melting, since at that temperature it exercises 1 atmosphere pressure, and the heat from the surroundings is used as heat of vaporization instead of being employed in raising the temperature to the melting-point (−56°).

The solid is used in the laboratory as a cooling agent, being often mixed with ether to give closer contact with the vessel. Mercury (m.-p. −40°) is easily frozen by the mixture.

Carbon dioxide gas (760 mm. and 15°) dissolves in its own volume of water. Up to four or five atmospheres Henry's law (p. 128) describes its solubility accurately. An aqueous solution, under a pressure of 3–4 atmospheres, is familiarly known as **soda water,** or carbonated water.

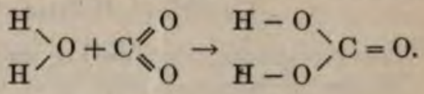
Chemical Properties. — Carbon dioxide is a stable compound. At 2000°, the dissociation reaches 1.8 per cent, or about the same as that of water: $2CO_2 \rightleftarrows 2CO + O_2$.

The more active metals, like magnesium, burn brilliantly when ignited in a hollow lump of solid carbon dioxide, producing the oxide and free carbon. Less active metals, such as zinc and iron, when heated in a stream of the gas, give an oxide of the metal and carbon monoxide (*q.v.*).

Carbon dioxide unites directly with many oxides, particularly those of the more active metals, such as the oxides of potassium, sodium, calcium, etc. Hence the decomposition of calcium carbonate by heating (p. 381) is a reversible action.

Carbon dioxide, when dissolved in water, forms an unstable acid:

$$H_2O + CO_2 \rightleftarrows H_2CO_3, \quad \text{or}$$



The name carbonic acid is frequently, though improperly, given to the anhydride CO_2, which has no acid properties.

Chemical Properties of Carbonic Acid H_2CO_3. — The solution of carbon dioxide in water exhibits the properties of a weak acid. It conducts electricity, although not well. It turns litmus red. The ionization takes place chiefly according to the equation:

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-.$$

Carbonates and Bicarbonates. — When excess of an aqueous solution of carbonic acid is mixed with a solution of a base like sodium hydroxide, or, as the operation is more usually performed, when carbon dioxide is passed into a solution of the alkali, until the liquid is saturated, water is formed and the acid carbonate (**bicarbonate**) of sodium remains dissolved:

$$H_2CO_3 + NaOH \leftrightarrows H_2O + NaHCO_3, \quad \text{or} \quad H^+ + OH^- \rightarrow H_2O.$$

Although the bicarbonate is technically an acid salt, its solution is neutral, on account of the exceedingly slight dissociation of the HCO_3^- ion. By addition of an equivalent of sodium hydroxide, the normal carbonate is obtained:

$$NaOH + NaHCO_3 \rightleftarrows H_2O + Na_2CO_3, \text{ or } OH^- + HCO_3^- \rightleftarrows H_2O + CO_3^=.$$

This solution, like that of all salts of a strong base and a feeble acid (*cf.* p. 271), is alkaline in reaction. This is because the tendency to form the very slightly ionized HCO_3^- makes the foregoing ionic action noticeably reversible (*cf.* pp. 271, 370).

The **normal carbonates**, with the exception of those of potassium, sodium, and ammonium, are insoluble in water, and may be obtained by precipitation when the proper ions are employed. For example:

$$BaCl_2 + Na_2CO_3 \rightleftarrows BaCO_3\downarrow + 2NaCl, \quad \text{or} \quad Ba^{++} + CO_3^{=} \rightleftarrows BaCO_3\downarrow.$$

The aqueous solution of carbon dioxide interacts with solutions of barium and calcium hydroxides in a similar manner:

$$Ca(OH)_2 + H_2CO_3 \leftrightarrows CaCO_3\downarrow + 2H_2O.$$

These precipitations are used as **tests** for carbon dioxide.

Excess of carbon dioxide converts calcium carbonate into the more soluble bicarbonate, and hence considerable quantities of "lime" (hardness, *q.v.*) are frequently held in solution by natural waters which contain carbon dioxide in solution:

$$H_2CO_3 + CaCO_3 \rightleftarrows Ca(HCO_3)_2.$$

In the same fashion, the carbonates of iron ($FeCO_3$), magnesium, and zinc are somewhat soluble in water containing free carbonic acid. In fact, the solution, transportation, and deposition of all these carbonates take place in nature on a large scale by the alternate progress and reversal of this action.

Uses of Carbon Dioxide. — The use of the gas for impregnating aerated waters has been mentioned. The gas is used in immense quantities in the manufacture of sodium bicarbonate $NaHCO_3$ (baking soda), of sodium carbonate $Na_2CO_3,10H_2O$ (washing soda), and of white lead, a basic carbonate of lead $Pb_3(OH)_2(CO_3)_2$.

Since carbon dioxide is already fully oxidized, it does not burn, and since it is very stable, ordinary combustibles will not burn in it. A small percentage of it will destroy the power of air to support combustion. For this reason, portable **fire extinguishers** contain a dilute solution of sodium bicarbonate, and a bottle of sulphuric acid. When the tank is inverted, the acid flows into the solution:

$$2NaHCO_3 + H_2SO_4 \rightleftarrows Na_2SO_4 + 2H_2CO_3 \rightleftarrows 2H_2O + 2CO_2.$$

The liquid is saturated with the gas and the excess, rising to the top, by its pressure forces the solution out through the nozzle. The liquid is more effective than an equal amount of water, because the carbon dioxide it carries mixes with the surrounding air.

The most wonderful chemical change which carbon dioxide undergoes is perhaps the most useful to mankind, and at the same time the one least understood. This is the action by which *plants use it as food* (see last section of this chapter).

CARBON MONOXIDE CO

Preparation. — In the laboratory, carbon monoxide is obtained by heating oxalic acid, a solid, white, crystalline substance, in a flask with concentrated sulphuric acid. The latter is here employed simply as a dehydrating agent (p. 286), so that it need not be included in the equation:

$$H_2C_2O_4 \rightarrow CO_2 + CO + H_2O.$$

To obtain pure carbon monoxide from this mixture, it is necessary to remove the carbon dioxide, by passing the gas through a solution of potassium hydroxide contained in a wash bottle. By using formic acid, or sodium formate, with sulphuric acid, the presence of the carbon dioxide is avoided:

$$HCHO_2 \rightarrow CO + H_2O.$$

We commonly observe the blue flame of burning carbon monoxide playing on the surface of a coal fire. The gas is produced by the passage of the carbon dioxide, which is first formed, through the upper layers of heated coal:

$$CO_2 + C \rightarrow 2CO.$$

A similar reduction of carbon dioxide is produced when the gas is led over a metal, such as zinc, and heat is applied:

$$CO_2 + Zn \rightarrow ZnO + CO.$$

Producer Gas and Water Gas. — When coke and *air* are used in the reaction mentioned above, the mixture of carbon monoxide (about 33 per cent) and nitrogen (about 66 per cent) obtained is called **producer gas.** It is combustible and is used in factories for heating and to drive gas engines for power.

When steam is driven through white hot coke or anthracite, a mixture of hydrogen and carbon monoxide, known as **water gas,** is produced·

$$C + H_2O \rightarrow CO + H_2 - 28{,}300 \text{ cal.}$$

The coke, piled in a brick-lined, cylindrical structure, is brought to vigorous combustion by blowing in air for ten minutes. Then steam is substituted for the air. Since the interaction takes place with absorption of heat (is endothermal, see equation), in about five minutes the coke becomes too cool. Air is then substituted for steam, and so on alternately. The gas is collected while the steam is turned on, and contains equal volumes of the two gases, together with some carbon dioxide (4–7 per cent), nitrogen (4–5 per cent) and oxygen (1 per cent). The gas is, therefore, almost wholly combustible and is used as a source of heat, and for driving gas engines to furnish power. It is used also for making illuminating gas (*q.v.*). Since carbon monoxide is more easily liquefied than is hydrogen, the latter gas is obtained, for commercial use, by passing water gas through a liquefier.

When both steam and air are driven *together* over burning coke, the latter is able to burn continuously, and a fuel gas which is a cross between producer gas and water gas is obtained.

Fuel gases are used on a large scale in steel works, and other factories. They give a uniform and easily regulated heat, they leave no ash, and their use involves no labor for stoking. As gases, also, they can be used in structures in which coal, as a solid, could not be employed.

Physical Properties. — Carbon monoxide is a colorless gas, with a metallic odor and taste (poisonous!). It is very slightly soluble in water. Its density is almost the same as that of air. When liquefied it boils at $-190°$.

Chemical Properties. — All the chemical properties of carbon monoxide are referable to the fact that in it the element carbon appears to be bivalent: $C=O$. The compound is in fact unsaturated, and combines with oxygen, chlorine, and other substances directly. Thus the gas burns in the air, uniting with oxygen to form carbon dioxide. Again, iron (*q.v.*) is manufactured by the reduction of the oxide of iron by gaseous carbon monoxide in the blast furnace:

$$Fe_2O_3 + 3CO \rightleftarrows 2Fe + 3CO_2.$$

In sunlight carbon monoxide unites directly with chlorine to form **carbonyl chloride** (phosgene) $COCl_2$. It unites with nickel and iron to form nickel carbonyl and iron carbonyl (*q.v.*), respectively.

The gas is an active poison. When inhaled it unites with the hæmoglobin of the blood, to the exclusion of the oxygen which forms a less stable compound (*cf.* p. 36). A quantity equivalent to about 10 c.c. of the gas per kilo. weight of the animal is sufficient to produce death, about one-third of the whole hæmoglobin having entered permanently into combination with carbon monoxide. One volume in 800 volumes of air produces death in about thirty minutes. This gas is the chief poisonous substance in illuminating gas. The poisonous effect of tobacco smoke, when inhaled, is partly due to the carbon monoxide produced by incomplete combustion. Nicotine, although contained in tobacco leaves, is unstable, and is decomposed by the heat. Traces of other irritant organic compounds, however, are contained in the smoke.

Carbon Dioxide as Plant Food. — The walls of the cells which form the framework of a plant are made of cellulose $(C_6H_{10}O_5)_x$. In the cells, especially those in certain parts of the plant, granules of starch $(C_6H_{10}O_5)_y$ are found. The plant contains also proteins. These substances contain carbon, hydrogen, oxygen, nitrogen, sulphur, and phosphorus, and plant food must furnish these elements. Compounds of potassium are also required. Hence, in addition to large amounts of water ascending through the roots and stem, carrying sufficient quantities of soluble compounds of the four elements last named, all plants require an abundant supply of carbon in absorbable form. Now, this comes from atmospheric carbon dioxide, admitted through minute openings situated mainly on the surfaces of the leaves. Comparison of the formulæ CO_2 and $C_6H_{10}O_5$ shows at once that the assimilation of the carbon dioxide of the plant must involve *reduction*. The chlorophyll (green matter) and protoplasm in the leaves act upon the carbon dioxide, causing oxygen gas to be liberated:

$$6CO_2 + 5H_2O + 671{,}000 \text{ cal.} \rightarrow C_6H_{10}O_5 + 6O_2.$$

This action goes on only in sunlight, and if green leaves are placed under water saturated with carbon dioxide, oxygen is given off and can be collected.

The enormous amount of energy absorbed in the action, and represented in terms of heat in the equation, is furnished by the sunlight. It may be added that plants, like animals, also use some oxygen and produce some carbon dioxide, but this process is entirely overborne in daylight, and is noticeable only in the dark.

The energy that does the world's work comes mainly from two sources, namely, water power and the combustion of wood or coal (which is fossil wood). The water comes from vapor, generated by the *sun's heat*, condensed as rain, and ultimately feeding the rivers. The source of the energy in wood and coal is now apparent. When wood, which is largely cellulose $(C_6H_{10}O_5)_x$, burns, it gives carbon dioxide, water, and heat. In fact, its combustion is represented by the above equation, *when read backwards*. Thus, the sunlight, through the machinery of the plant, takes carbon dioxide and water, supplies the energy (as light), and gives us wood and oxygen. And the wood and oxygen, when burned, give us back the original substance, and the equivalent of the original energy in the form of heat. Thus, the two sources of energy turn out to be the same, namely the sun's rays.

If, instead of burning the starch of the plant, we consume it as food, it goes through *several* changes instead of one. But the final products are the same, namely carbon dioxide and moisture, given off through our lungs and skin, and heat and other forms of energy such as are developed in animals. Thus, whether we use our muscles, a steam engine, or a water turbine to do work, sunlight is in each case the ultimate source of the energy employed.

Exercises. — 1. To which two factors in the interaction of calcium carbonate and hydrochloric acid (p. 381) is due the forward displacement of all the equilibria?

2. What will be the excess of pressure inside a bottle of soda water when 4 vols. carbon dioxide are dissolved in 1 vol. water?

3. What volume of liquid carbon dioxide, measured at 0°, will be required to give 75 liters of the gas at 0° and 760 mm. pressure?

4. What are the exact relative weights of equal volumes of carbon dioxide, carbon monoxide, air, and steam?

CHAPTER XXIX

THE HYDROCARBONS. ILLUMINANTS. FLAME

The compounds of carbon and hydrogen are called the hydrocarbons. Hundreds of different hydrocarbons, containing different proportions of the two elements are known. The natural oil petroleum is a mixture of many substances of this class.

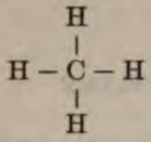
The hydrocarbons fall into several distinct series, the chief one of which contains methane CH_4 as its simplest member. On account of the fact that certain members of this set are found in paraffin, it is commonly known as the **paraffin series.** For the reason that in this series the carbon has all its four valences employed, the members are also called the **saturated hydrocarbons.**

Paraffin or Saturated Series of Hydrocarbons. — The following is a list of the names, formulæ, and boiling-points of seven of the simplest hydrocarbons of this series, and of two of the higher members of the series:

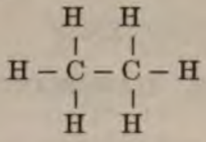
Methane	CH_4	b.-p.	−164°	Hexane	C_6H_{14}	b.-p	71°
Ethane	C_2H_6	"	− 89.5°	Heptane	C_7H_{16}	"	99°
Propane	C_3H_8	"	− 37°	Hexadecane	$C_{16}H_{34}$	"	287.5°
Butane	C_4H_{10}	"	+ 1°	"	"	m.-p.	18°
Pentane	C_5H_{12}	"	35°	Pentatricontane	$C_{35}H_{72}$	"	74.7°

After the first four, the names are based on the Greek numerals representing the number of carbon atoms in the molecule. Heptane is followed by octane C_8H_{18}, nonane C_9H_{20}, decane $C_{10}H_{22}$, etc. On examining the formulæ, we perceive that, in each, the number of hydrogen atoms is equal to twice the number of carbon atoms plus two. The general formula is therefore C_nH_{2n+2}. The series illustrates strikingly the law of combining weights (p. 42). We note, also, that the **first four are gases** at room temperature. The members from pentane to pentadecane $C_{15}H_{32}$ are **liquids,** and from hexadecane onwards they are **solids.**

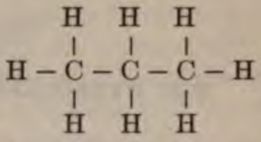
In these compounds the carbon is quadrivalent, and each substance is related to the preceding one by containing the additional units CH_2. The graphic formulæ of the first three members illustrate these two facts:



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

These hydrocarbons are extremely indifferent in their **chemical behavior.** They have none of the properties of acids, bases, or salts. The halogens, notably chlorine and bromine, however, interact with them (see below). When burned they all produce carbon dioxide and water.

Petroleum. — Petroleum is a thick, often greenish-brown colored oil. When borings reach the oil-bearing strata, the oil, hitherto held beneath impervious strata, and often under hydrostatic pressure of water underneath or around it, either gushes up or is pumped to the surface. Wells are in operation in Caucasia, Gallicia, India, Japan, and in Ontario, Ohio, Pennsylvania, California and elsewhere in North America. The world's production in 1912 was 350 million barrels (42 gal. each), of which nearly 220 millions were produced in the United States.

The oil is a complex mixture, and is *partially* separated by distillation (p. 93) into products which are still mixtures, but are suited to special purposes. The components of lower boiling-point come off first and the temperature rises steadily as these components are eliminated and those of higher and higher boiling-point enter the vapor. As certain temperatures are reached (or as the sp. gr. of the distillate attains certain values) the condensed liquid is diverted into different vessels, so as to collect together the "fractions" of the same kind. This is called **fractional** distillation.

At some suitable stage, the residual oil is chilled, and a quantity of the solid members of the series ($C_{22}H_{46}$ to $C_{28}H_{58}$) crystallizes in flakes (solid **paraffin**) and is separated by filtration in presses. The final residue is used for lubricants and for fuel. The fractions are still mixtures, but contain mainly compounds lying close together in the series. Some of the products are as follows:

Name.	Components.	B.-P.	Uses.
Petroleum ether	Pentane, hexane	40°– 70°	Solvent, gas-making
Gasoline	Hexane, heptane	70°– 90°	Solvent, fuel
Naphtha	Heptane, octane	80°–120°	Solvent, fuel
Benzine	Octane, nonane	120°–150°	Solvent
Kerosene . . .	Decane-hexadecane	150°–300°	Illuminating-oil

Petrolatum (vaseline), $C_{22}H_{46}$ to $C_{23}H_{48}$, is separated in some refineries. Solid **paraffin** is employed in waterproofing paper, as an ingredient in candles, in the laundry, and to cover preserves. **Kerosene,** for oil lamps, is usually the largest fraction. To be used safely, it should not give any inflammable vapor below 65° (150° F.), which is the legal flash-point in many states. Special treatment, such as superheating the vapor under high pressure (Rittman's process), is used to increase the proportion of **gasoline** (petrol) for which there is a large and increasing demand.

Asphalt, a natural mixture of solid hydrocarbons found particularly in Trinidad, is used in road-making.

Methane CH_4. — Methane is the chief component of **natural gas** (over 90 per cent), which, like the oil, is confined beneath impervious strata and is forced out through borings by hydrostatic pressure. It is found mainly in or near the localities where oil is found. It also rises to the surface when the bottoms of marshy pools are disturbed (**Marsh-gas**), and issues from seams in coal beds as **fire-damp** (Ger. *Dampf*, vapor). In these two cases it results from the decomposition of vegetable matter in absence of air. Its *formation* by direct union of carbon and hydrogen has already been discussed (p. 378).

Methane may be **made** from inorganic materials by the action of water upon aluminium carbide, prepared by the interaction of aluminium oxide and carbon in the electric furnace (*cf.* pp. 378, 377):

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4.$$

In the *laboratory* the gas is commonly obtained by the distillation of a dry mixture of sodium acetate and sodium hydroxide:

$$NaCO_2CH_3 + NaOH \rightarrow Na_2CO_3 + CH_4.$$

As regards **chemical properties**, methane, like other saturated hydrocarbons (p. 390), is very indifferent. When a mixture of methane and chlorine is exposed to sunlight several changes occur in succession (*cf.* p. 162):

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl, \quad CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl,$$
$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl, \quad CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl.$$

This kind of interaction with the halogens is characteristic of compounds of hydrogen and carbon. It takes place slowly, and is therefore entirely different from ionic chemical change. It consists in a progressive **substitution** of chlorine for hydrogen, unit by unit. **Chloroform** $CHCl_3$ and carbon tetrachloride CCl_4 (p. 379) are familiar substances. The iodine derivative, **iodoform** CHI_3 is used in surgical dressing. These substances are not salts, and are not ionized in solution. They are very slowly hydrolyzed by water — carbon tetrachloride, for example, giving carbonic acid and hydrochloric acid.

Methane and the other saturated hydrocarbons are decomposed by strong heating (see cracking, below).

Unsaturated Hydrocarbons. — In addition to the saturated series of hydrocarbons, several other series are known in which smaller proportions of hydrogen are present. Thus, **ethylene** C_2H_4, to which illuminating gas largely owes the luminosity of its flame, belongs to a series C_nH_{2n}, all the members of which contain two atoms of hydrogen less than the corresponding compounds of the first series. Again, **acetylene** C_2H_2 is the first member of a series C_nH_{2n-2}, and **benzene** C_6H_6 begins a series C_nH_{2n-6}, of which **toluene** C_7H_8 (p. 349) is the second member.* These are all unsaturated because the full valence of the carbon is not in use, and these compounds, therefore, unite more or less readily with hydrogen, chlorine, bromine, and concentrated sulphuric acid. The hydrocarbons of all the series are mutually soluble, but none of them dissolve in water.

Members of the ethylene and acetylene series are found in petroleum, and are formed also to some extent by decomposition during the distillation. As oil containing them acquires dark-colored products by chemical change, the oils are always refined before being sold. They are agitated with concentrated sulphuric acid, which unites with the unsaturated substances and, being insoluble in the oil, collects in a layer below it. The oil is finally washed free from the acid with dilute alkali and with water.

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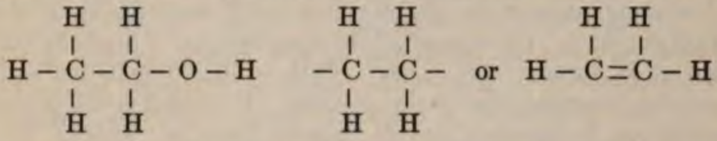
* Isoprene C_5H_8, a member of the unsaturated series C_nH_{2n-2}, when heated in presence of sodium (or some other contact agent), changes into caoutchouc $(C_5H_8)_x$ or raw rubber. No method of preparing synthetic rubber has yet been used commercially.

Ethylene C_2H_4. — Ethylene is the first member of the second series of hydrocarbons. It corresponds to ethane C_2H_6, but contains in each molecule two hydrogen units less than does this substance.

Ethylene is **made** by heating common alcohol (ethyl alcohol) with concentrated sulphuric acid:

$$C_2H_5OH \rightarrow H_2O + C_2H_4\uparrow.$$

A comparison of the graphic formulæ of the alcohol and ethylene shows that this loss of water leaves the carbon partly unsaturated:



$$\begin{array}{c} HH \\ |\,| \\ H-C-C-O-H \\ |\,| \\ HH \end{array} \qquad \begin{array}{c} HH \\ |\,| \\ -C-C- \\ |\,| \\ HH \end{array} \quad \text{or} \quad \begin{array}{c} HH \\ |\,| \\ H-C=C-H \end{array}$$

The elements of water may also be removed by allowing the alcohol to fall drop by drop onto heated phosphoric anhydride.

Ethylene is formed, along with acetylene and other substances, when any saturated hydrocarbon is heated strongly. Even methane gives it:

$$2CH_4 \rightarrow C_2H_4 + 2H_2.$$

Ethylene is a gas. It burns in the air with a flame which, on account of the great separation of free carbon which takes place temporarily during the combustion (*cf.* Flame), is highly luminous. It will be seen that, in the formula, but three of the valences of each carbon unit are occupied: the substance is unsaturated. Hence, when ethylene is passed through liquid bromine it is rapidly absorbed, and the bromine seems to increase in volume and finally loses all its color, being converted into a transparent liquid having the composition $C_2H_4Br_2$, **ethylene bromide.**

Acetylene. — This substance, likewise a gas, is the first member of still another unsaturated series. Its formula C_2H_2 shows that its molecule lacks four of the hydrogen units necessary to the complete saturation which we find in ethane. Graphically its structure is usually represented thus: $H - C \equiv C - H$. This gas is formed in small quantities by direct union of carbon and hydrogen in the electric arc (p. 378). This is because the reaction is endothermal (p. 189). For the same reason, it is also produced when ethylene is passed through a heated tube: $C_2H_4 \rightarrow C_2H_2 + H_2$ (*cf.* Flame).

When calcium carbide (p. 379) is thrown into water it is hydrolyzed. Violent effervescence occurs, the calcium carbide is disintegrated, a precipitate of calcium hydroxide is formed, and acetylene passes off as a gas:

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2.$$

This action is like that of water on calcium phosphide (p. 365), magnesium nitride (p. 339), and aluminium carbide (p. 391).

Acetylene burns with a flame which is still more luminous than that of ethylene. On account of the large amount of heat absorbed when it is formed: $2C + H_2 \rightarrow C_2H_2 - 53{,}200$ cal., an equal amount is liberated when it decomposes. If the gas is compressed in tanks, it is therefore apt to explode from any shock. It is frequently made in generators, as needed, by the foregoing action, and is used for lighting on automobiles and in regions remote from a public supply of illuminating gas. The acetylene tanks, which are also in use, contain acetylene dissolved under high pressure in acetone, a form in which it can be handled safely.

When acetylene C_2H_2 is burned, we obtain from $2 \times 12 + 2 = 26$ g. not only the heat due to the combustion of the carbon ($2 \times 12 \times 8040$ cal., p. 376), and of the hydrogen ($2 \times 28{,}800$ cal.), but also the heat due to the decomposition of the gas (53,200 cal.). The temperature of the flame is therefore extraordinarily high. The oxyacetylene flame, produced by means of a suitable burner (Fig. 32, p. 58), is now used, under the name of the **acetylene torch,** for cutting metals. The gases are contained in portable tanks. Such a flame will melt its way through a 6-inch shaft or a steel plate several feet wide in less than a minute, cutting the object in two. Steel buildings have thus been taken down, and ships (like the *Maine*) have been cut up for removal. Other gases, like blau gas and oil gas, made by cracking petroleum (see below), are now displacing acetylene for this purpose, as they are almost as effective, and the flame is more easily controlled.

Cracking of Hydrocarbons. — All hydrocarbons, when heated strongly (air-excluded) decompose or **crack.** The changes seem to be reversible, and the result therefore depends upon the conditions. Thus, at atmospheric pressure, and especially when the oil is mainly present as a liquid, hydrogen is given off and unsaturated liquid and gaseous hydrocarbons are produced. Under such conditions, ethylene is formed in large amounts. On the other hand, when an oil free from gasoline is completely vaporized (500°), and is under high pressure, the hydrogen is forced into combination with the broken molecules and the saturated constituents of gasoline are produced in large amount (Rittman's process).

At a white heat, all the hydrocarbons decompose into hydrogen and free carbon. The latter is deposited in a dense form called **gas-carbon,** which is more or less crystalline (like graphite) and used in making carbon rods for arc lights and electric furnaces, and carbon plates for batteries, and for the electrodes employed in electrolysis. The carbon is ground up, moistened with petroleum residues, subjected to hydraulic pressure and finally heated strongly to expel volatile matter.

Carburetted Water Gas. — As we have seen, water gas is essentially $H_2 + CO$ (p. 386), and burns with a pale-blue flame. To fit it for use as illuminating gas, unsaturated hydrocarbons, which burn with a luminous flame, such as ethylene C_2H_4 and acetylene C_2H_2 must be added. The gas is sent through a tower containing strongly heated brick on which a petroleum oil is sprayed. Mixed with the vapor, the gas then passes into the "superheater" where, at a higher temperature, the cracking into unsaturated hydrocarbons occurs. The gas is then cooled and washed to remove condensible hydrocarbons, which would otherwise obstruct the service pipes. A typical carburetted water gas has the composition: Illuminants 17 per cent; heating gases, methane 20 per cent, hydrogen 32 per cent, carbon monoxide 26 per cent; impurities (nitrogen and carbon dioxide) 5–6 per cent. A flame burning 5 cu. ft. per hour gives 25 candle power.

Blau gas and **Oil gas,** such as Pintsch gas, contain larger proportions of illuminants. Thus a good oil gas shows: illuminants 45 per cent; heating gases, methane 39 per cent, hydrogen 14.5 per cent; impurities 1.5 per cent; candle power 65. Such gases are compressed in tanks and used for illumination on railway trains (Coal gas, see p. 410).

FLAME

Meaning of the Term. — In the combustion of charcoal there is hardly any **flame,** for the light emanates almost entirely from the incandescent, massive solid. When two gases are mixed and set on fire, a sort of flame passes through the mixture, but this can hardly be accounted a flame, in the ordinary sense, either. The rapid movement of the flash, and the explosion which accompanies it, are in a manner the precise opposite of the quiet combustion which is characteristic of flames.

With illuminating gas the production of its very characteristic flame is due to the chemical union of a stream of one kind of gas in an atmosphere of another. The flame is made up of the heated matter where the two gases meet. In the case of a burning candle (Fig. 102), one of the bodies appears to be a solid, but a closer scrutiny of the phenomenon shows that the solid does not burn directly. A combustible gas is manufactured continuously by the heat of the combustion and rises from the wick. The introduction of a narrow tube into the interior of the flame enables us to draw off a stream of this gas and to ignite it at a remote point. Thus, **a flame is a phenomenon produced at the surface where two gases meet and undergo combination with the evolution of heat and, more or less, light.**

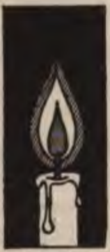


FIG. 102.

In the chemical point of view, it is a matter of indifference whether the gas outside the flame contains oxygen, and the gas inside consists of substances ordinarily known as combustibles, or whether this order is reversed. In an atmosphere of ordinary illuminating gas, the flame must be fed with air. This condition is easily realized (Fig. 103). The lamp chimney is closed at the top until it has become filled with illuminating gas. This can be ignited as it issues from the bottom of the wide, straight tube. When the hole in the cover of the lamp chimney is then opened, the upward draft causes the flame of the burning gas to recede up the tube, and there results a flame fed by air and burning in coal gas.

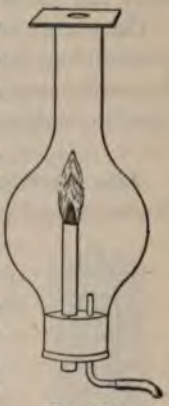


FIG. 103.

Luminous Flames.—The flame of hydrogen, under ordinary circumstances, is almost invisible, nearly all the energy of the combustion being devoted to the production of heat. A part of this, however, may be transformed into light by the suspension of a suitable solid body, such as a platinum wire, in the flame. The holding of a piece of quicklime in an oxyhydrogen flame (*cf.* p. 58) is a practical illustration of this method of securing luminosity. In general, luminosity may be produced by the presence of some solid which is heated to incandescence.

In the Welsbach lamp the flame itself is nonluminous and, but for the mantle, would be identical with the ordinary Bunsen flame. The mantle which hangs in the flame, however, by its incandescence, furnishes the light. This mantle is composed of a mixture of 99 per cent thorium dioxide ThO_2 and one per cent cerium dioxide CeO_2. These oxides act as a contact agent, hastening the combustion and liberation of heat close to their surface, and so acquire a temperature higher than the average for the rest of the flame. The Welsbach lamp gives four times as much light as does the same gas, issuing at the same rate, from an ordinary burner.

In cases of brilliant combustion, as of magnesium ribbon or phosphorus, a solid body is formed whose incandescence accounts for the light. The flame of ordinary illuminating gas does not at first sight appear to give evidence of the presence of any solid body. But if a cold evaporating dish is held in the flame for a moment, a thick deposit of finely divided carbon (soot) is formed, and we at once realize that the light is due to the glow of these particles in a mass of intensely hot gas. Carbon is, indeed, an extremely combustible substance, and is eventually entirely consumed. But a fresh supply is being generated continuously in the interior of the flame, while the oxygen with which it is to unite is outside the flame altogether. Thus the carbon particles persist until, drifting with the spreading gas, they reach the periphery of the flame.

On a large scale, oil residues are burned so that the flame strikes a revolving, iron vessel cooled with water. The soot or **lampblack** is continuously scraped off as the vessel turns. Lampblack is used in making printer's ink, India ink, and black varnish.

The Bunsen Flame. — In the burner devised by Robert Bunsen, a jet of ordinary illuminating gas is projected from a narrow opening into a wider tube (Fig. 104). In this tube it becomes mixed with air, entering through openings whose dimensions can be altered by means of a perforated ring. When the supply of air is sufficient, the flame becomes non-luminous. With a somewhat different construction, and the use of a bellows to force a larger proportion of air into the gas, a still hotter flame can be produced. The instrument in this case is known as a **blast lamp.**

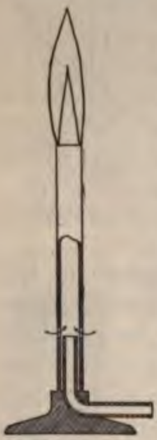


FIG. 104.

The high temperature of the **blast lamp flame** presents an interesting problem. The same amounts of gas and air burn to give the same amounts of the same products, whether the air blast is on or off. The same amount of heat is produced, and the same quantities of the same substances are heated. The average temperature throughout the flame should therefore be the same. In point of fact, it is the same, but the stream of hot gas is *moving more rapidly* when the blast is going. The temperature of a body immersed in the flame depends, on the one hand upon the rate at which heat reaches it, and upon the other on the rate at which it loses heat by radiation. The heat is partly carried by the moving, heated gases (convection), and partly transmitted by conduction through the *stationary layer* (p. 331) on the surface of the body. Now, the latter is the slower process. Hence a rapid stream of gas, which leaves a thinner stationary layer, will diminish the distance the heat has to travel by conduction and so convey heat to the body faster than could a slow stream of the same temperature. Thus, with a blast flame, the loss by radiation is the same at the same temperature, but heat reaches the body faster and so the temperature of the body more nearly approaches that of the flame itself.

Structure of the Illuminating and the Bunsen Flame. — When an exceedingly small luminous flame is examined, the various parts of which it consists may easily be made out. In the interior there is a dark cone which is composed of illuminating gas and air, and in it no combustion is taking place. A match-head may be held here for some time without being set on fire. This is therefore not properly a part of the flame. Outside this is a vivid blue layer (*C*, Fig. 105) which is best seen in the lower part of the flame, but extends beneath the luminous sheath, and covers the dark inner cone completely. Outside the blue flame, and covering the greater part of it, is the cone-shaped luminous portion (*B*). Over all is a faint mantle of non-luminous flame (*A*), which becomes visible only when the light from the luminous part is purposely obstructed. In the luminous gas-flame, therefore, there are four regions, if we count the inner cone of gas. The difference between this and the non-luminous Bunsen flame is that in the latter the luminous region is omitted, and the inner, dark cone, the blue sheath, and the outer mantle, are the only parts which can be distinguished.

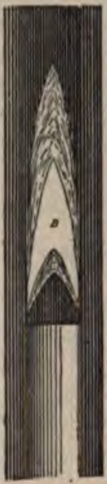


Fig. 105.

The Causes of Luminosity and Non-Luminosity. — The study of the chemical changes taking place in the Bunsen flame, particularly with the object of explaining (1) the luminosity of the flame of the pure gas, and (2) the non-luminosity of that produced by the same gas when it is mixed with air, has been the subject of many elaborate investigations. The questions are: (1) Why is carbon liberated in the former case, and (2) why is it not liberated in the latter? Let us consider these questions in order.

1. The investigations of Lewes (1892) and others show conclusively that the free carbon in the luminous zone of the ordinary flame is accompanied by free hydrogen, and that both are formed by dissociation of the ethylene. This substance, when heated,

gives acetylene, and the latter then dissociates into carbon and hydrogen (p. 394):

$$C_2H_4 \rightarrow H_2 + C_2H_2 \rightarrow 2C + H_2.$$

The carbon glows, until, as it drifts outwards, it encounters the oxygen of the air and is burned. The first oxygen encountered combines more readily with the hydrogen, since it is a gas, than with the carbon, which is now in *solid* particles and therefore burns less readily. That carbon glows when heated in the absence of oxygen, without being consumed, is a fact familiar in the behavior of the incandescent electric lamp, the filament of which is often made of carbon.

The conception that when hydrocarbons burn, they first undergo dissociation, and then union with oxygen, is in harmony with what we have observed also in the case of the combustion of hydrogen sulphide, where the presence of free sulphur and free hydrogen in the interior of the flame was demonstrated (p. 268).

2. The influence of the air admitted to the Bunsen burner, in interfering with this dissociation in such a way as to destroy all luminosity, is the most difficult point to explain. The effect is frequently attributed to the oxygen which the air contains. This view, however, is seriously weakened by a consideration of the undoubted fact that oxygen is not required. Carbon dioxide and steam are equally efficient when introduced instead of air (Fig. 106, gas enters at *a* and CO_2 at *b*). Even nitrogen, which cannot possibly be suspected of furnishing any oxygen, likewise destroys the luminosity. Lewes has shown that 0.5 volumes of oxygen in 1 volume of coal gas destroy the luminosity. But 2.30 volumes of nitrogen or 2.27 volumes of air accomplish the same result. Thus the efficiency of air is not much greater than that of nitrogen, in spite of the fact that one-fifth of the former is oxygen.

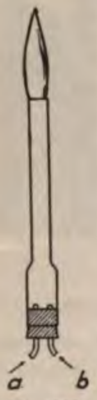


Fig. 106.

It is evident that the effect is due, in part at least, to the *dilution* with a *cold* gas. This is confirmed by the observation that a cold platinum dish held in a small luminous flame is similarly destructive of the luminosity. If the tube of the Bunsen burner is heated so that the mixed gases are considerably raised in temperature before reaching the non-luminous flame, the latter becomes luminous. It is probable, therefore, that the cold gas lowers the temperature of the inner flame, and at the same time the dilution diminishes the speed with which the free carbon is formed (Lewes). Even if the temperature is not reduced below that at which dissociation of the ethylene can occur, yet the dilution and cooling, together, prevent that sharp dissociation at this particular point which is necessary for the production of the great excess of free carbon needed to furnish the light.

Before these investigations were made, a different answer was given to the question why the flame of pure illuminating gas contains free carbon and is luminous. It was said that hydrogen was more easily burned than carbon, and therefore the latter was left free, to be burned later. It is true that gaseous hydrogen burns more easily than *solid* carbon, *e.g.*, charcoal. But in ethylene, *both* elements are equally gaseous and the explanation is faulty. Smithells (1892) demonstrated the falsity of this explanation by devising a **cone-separator** (Fig. 107). The air and ethylene or other gas are admitted separately, and the inner cone of the non-luminous flame rests on the inner, narrow tube, while the outer cone is at the top. By means of a side tube (not shown) he withdrew the inter-conal gas and found that, while all of the carbon was burned by the inner cone as far as carbon monoxide CO, most of the hydrogen was still entirely uncombined. The change in the inner cone of the Bunsen flame consists, therefore, mainly in the burning of all the hydrocarbons to carbon monoxide, with liberation of the hydrogen. In the outer cone, it is practically a burning of water gas that is taking place.

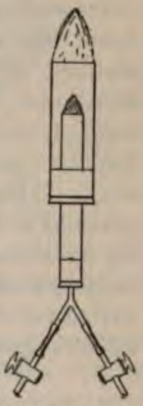


FIG. 107.

Exercises. — 1. Write a graphic formula for hexane.

2. Write an equation for the formation of aluminium carbide (p. 391).

3. Make a section showing the shape of the flame produced by burning hydrogen gas when the latter issues from a circular opening.

CHAPTER XXX

THE CARBOHYDRATES AND RELATED SUBSTANCES

A PLANT takes carbon dioxide from the air and water from the ground and, using the energy of sunlight, converts them into a growing framework of cellulose $(C_6H_{10}O_5)_y$ and, as we have seen (p. 387), into starch $(C_6H_{10}O_5)_z$ which it stores in the cells. The cellulose of certain plants furnishes us with cotton, linen, jute, and paper. The starch of wheat, oats, maize (corn), and potatoes is one of the chief foodstuffs they contain. The plant, when dead and buried, changes into coal. The fresh wood, when distilled, supplies wood spirit (methyl alcohol) and other useful substances, and the residue is the valuable charcoal. Furthermore, from starch we can readily make sugar, alcohol, and other familiar materials. Cellulose, starch, and the sugars (*e.g.*, cane-sugar $C_{12}H_{22}O_{11}$) contain oxygen and hydrogen in the same proportions in which they are present in water, 2H : 1O. They might be considered hydrates of carbon, and so they are called the **carbohydrates.** The foregoing brief summary shows that the carbohydrates introduce us to a much greater variety of interesting organic compounds than does petroleum.

Cellulose* $(C_6H_{10}O_5)_x$ *and Paper.—The wall of each cell, and therefore the whole framework of a plant, is made of cellulose. Linen and cotton are pure cellulose. The walls of the cells are usually more or less thickened by a substance called **lignin,** which has much the same composition, but different chemical behavior. The best paper is made of cotton or linen (rag-paper). Cheaper kinds are prepared by cutting wood, such as spruce or pine, into chips and treating ("cooking") them with a solution of calcium bisulphite $Ca(HSO_3)_2$. This process decomposes the lignin, and converts it into soluble materials. The sulphite liquor is then run off, and the pulpy material is washed, beaten with water to reduce it to minute shreds, and bleached with very dilute chlorine-water. The pure cellulose, now **paper-pulp,** is suspended in water, spread on screens, pressed, and dried. During the process, other substances are added. Thus, size (gelatine or rosin and alum, see Sizing) prevents the ink from running; pulverized calcium sulphate (gypsum), clay, and other white solids ("loading") give body to the paper and permit the production of a smooth surface by rolling ("calendering"). Dyestuffs can be added to give special tints. Filter paper is pure cellulose.

Starch $(C_6H_{10}O_5)_y$. — Starch consists of little colorless granules of various rounded shapes (Fig. 108), which are easily seen under the microscope. These granules are massed in large quantities in the ears of wheat and oats, in the tubers of potatoes, in the grains of maize (corn), and in peas and beans. Even in the leaves they can be seen. Starch is recognized by the iodine test (p. 3), turning deep blue with a trace of free iodine.

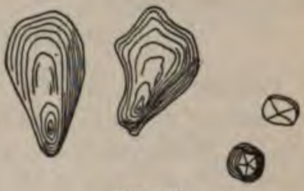


FIG. 108.

The treatment of wheat flour, which is three-fourths starch, by washing out the starch through a porous cloth with water, has already been described (p. 3). It is made from maize in America and from potatoes in Europe, by washing the flour on sieves.

Starch is *not* soluble in water. If boiled with water, however, the granules swell and break and the starch is diffused through the water, giving a clear liquid. If too much water is not used, the liquid when cold sets as a jelly. While the liquid is hot, much of the starch will pass through a filter along with the water. Such a liquid is called a **colloidal suspension.** Suspensions like this are constantly met with in using complex organic compounds like jellies, glues, soaps, and dyes. Even insoluble inorganic materials, like gold, give such suspensions (see p. 416).

The colloidal suspension of starch turns blue when a solution containing free iodine is added to it. It is **used** in the laundry for stiffening white goods. Glucose is manufactured from it.

Glucose $C_6H_{12}O_6$, ***a Sugar, from Starch.*** — When starch is boiled with water, to which a few drops of an acid (contact agent), such as hydrochloric acid, have been added, the liquid, after neutralization of the acid, is found to be sweet. One of the sugars, glucose $C_6H_{12}O_6$, can be obtained in crystals after evaporation. The crystals form "brewers' glucose" and the syrup produced by concentration is **corn syrup** (if maize is the source of the starch). The latter, although less sweet than ordinary sugar, is much less expensive and is used in making preserves and cheap candy.

The molecular weight of starch is unknown, but undoubtedly large. The formula $(C_6H_{10}O_5)_y$ shows the composition. The water, in presence of a little acid, decomposes the molecules and combines with the material. First, dextrin (used as paste or mucilage) is formed and this breaks up into glucose. The action is an hydrolysis:

$$(C_6H_{10}O_5)_y + yH_2O \rightarrow yC_6H_{12}O_6.$$

Glucose is known also as **dextrose** and as **grape sugar.** The crystalline granules in raisins (dried grapes) are composed mainly of it. When pure, it is almost colorless. It reduces cupric hydroxide, in Fehling's solution (*q.v.*), to cuprous oxide.

Corn syrup contains 30–40 per cent of unchanged dextrin, 40–50 per cent of glucose, and the rest water.

The Sugars. — The common sugars may be divided into the **monosaccharides,** usually with the formula $C_6H_{12}O_6$, and the **disaccharides,** usually $C_{12}H_{22}O_{11}$. Of these, the following will be referred to in what follows:

Monosaccharides:	**Glucose** (grape sugar or dextrose) $C_6H_{12}O_6$,
	Fructose (fruit sugar or levulose) $C_6H_{12}O_6$.
Disaccharides:	**Sucrose** (cane-sugar, beet-sugar) $C_{12}H_{22}O_{11}$.
	Maltose (action of malt on starch) $C_{12}H_{22}O_{11}$.
	Lactose (milk sugar, in animals only) $C_{12}H_{22}O_{11}$.

Sucrose, or Cane Sugar. — Plants, such as the sugar-cane and beet, besides forming cellulose and starch, produce exceptional amounts of **sucrose,** or table sugar. The sap of the sugar maple contains much of it.

Cane sugar is extracted by crushing the stalks between rollers, and evaporating the expressed liquid (18 per cent sugar) in closed pans. A partial vacuum is maintained so that the solution may boil at a low temperature (65° to begin with) and none of the sugar be decomposed. When the syrup cools, the sucrose appears in brown-colored crystals. The mother-liquor is called **molasses.** In the refinery, the sugar is redissolved, the solution is poured through a column of charcoal, which takes out the coloring matter, and the liquid is once more allowed to deposit crystals. Pure cane-sugar has a faint yellow tint, and a small amount of ultramarine (*q.v.*) is added to give that whiteness which is popularly connected with purity in sugar.

Sugar beets (16 per cent or more sugar) are sliced and steeped in water. The extract contains a gummy material in colloidal suspension. This is coagulated and precipitated by adding slaked lime (calcium hydroxide) $Ca(OH)_2$ suspended in water, and boiling. After separation of the clear liquid, carbon dioxide is passed through it to precipitate the excess of lime as carbonate ($CaCO_3$). The solution is then decolorized with charcoal and evaporated to crystallization.

As regards **properties,** sucrose crystallizes in four-sided prisms (rock-candy, Fig. 48, p. 83) and melts at 160°. When heated to 200–210° it partially decomposes, leaving a soluble, brown, mixed material, **caramel,** used in coloring whisky and soups. Sucrose does *not* reduce Fehling's solution.

When boiled with water containing a trace of acid (contact agent), sucrose is hydrolyzed, giving a mixture of the two monosaccharides, glucose and fructose:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6.$$

The mixture is called **invert sugar,** and is found in many sweet fruits and in honey. Each sugar interferes with the crystallization of the other, by lowering the freezing point (p. 134), and so invert sugar is added in making fondant candy and candy that is to be pulled, both of which must remain soft for some time. Icing for cakes has to some extent this property, and is made by adding acid substances to sugar, such as vinegar, lemon juice, or cream of tartar.

Enzymes. — Yeast, consisting of microscopic cells, belongs to a low order of plants. Its use lies in the fact that, while multiplying, it secretes within each cell two very active, soluble substances. These are **zymase** and **sucrase** (invertase) which belong to a class of organic substances called **enzymes.** Sucrase means an enzyme that splits sugar. Enzymes produce remarkable chemical changes by their mere presence (contact actions).

Alcoholic Fermentation. — When some yeast, which is a mass of the living plants, is added to a solution of glucose at about 30°, the small amount of zymase gradually decomposes the sugar. Bubbles of carbon dioxide soon begin to rise, and may be tested (p. 384) with limewater (Fig. 109). At the same time, alcohol (ethyl alcohol C_2H_5OH) accumulates in the liquid:

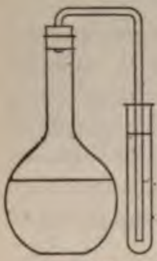


FIG. 109.

$$C_6H_{12}O_6 \rightarrow 2CO_2\uparrow + 2C_2H_5OH.$$

Yeast will ferment fructose $C_6H_{12}O_6$ with the same result, but more slowly, so that, when placed in invert sugar, it decomposes the glucose first and the fructose afterwards.

Zymase does not act upon sucrose (table sugar), but sucrase hydrolyzes the sucrose in the same way as does a dilute acid, giving invert sugar. The latter is then decomposed by the zymase, and so cane-sugar in solution is fermented by yeast into alcohol and carbon dioxide, just as is glucose, only more slowly.

In making **wine** the glucose contained in the grape juice is fermented by a species of yeast found on the skins of the grapes.

Commercial Alcohol is not made from sugar, but from the starch of potatoes or maize. When barley is allowed to sprout, an enzyme, **amylase** (meaning starch-splitting enzyme) or diastase, is formed in the ears. The whole material is dried, and is then called **malt.** When this is mixed with starch and water, the amylase hydrolyzes the starch to maltose $C_{12}H_{22}O_{11}$ (p. 404). The latter is then further hydrolyzed by yeast to form glucose $C_6H_{12}O_6$, and this is decomposed by the zymase into alcohol and carbon dioxide.

Whisky (about 50 per cent alcohol) is made by treating the starch of rye, maize or barley in the same way, with subsequent distillation (see below) to separate the alcohol (whisky). **Beer** is made similarly from various kinds of grain, especially barley, but the fermented liquor is not distilled.

Ethyl Alcohol C_2H_5OH.—Common alcohol is related to ethane C_2H_6, having an hydroxyl group in place of one unit of hydrogen. Hence its name, *ethyl* alcohol.

Ethyl alcohol boils at 78.3° and so, when the fermented liquor is distilled, it is almost pure alcohol that comes off. Commercial alcohol contains 95 per cent by volume (in Great Britain, 90 per cent). **Absolute alcohol** is made by adding quicklime, which combines with the water, and redistilling the liquid.

Alcohol mixes with water in all proportions. In dilute, aqueous solution it is not ionized, and does not interact with acids, bases, or salts. It is, however, easily oxidized to acetic acid. When water is absent, it interacts with acids slowly (see p. 413).

Alcohol is used as a solvent for the resins employed in making varnishes for wood and lacquers for metal.

On account of the high duty on 95 per cent alcohol ($2.11 per gallon in the U. S. and 24/6 in Gt. Britain), **denatured alcohol** (methylated spirit), which is free of duty, is employed for industrial purposes. The alcohol (cost about 22 cents per gal. in the U. S. and 1/6 in Britain) is mixed with offensive or poisonous materials, which prevent its consumption as a beverage, without interfering with other uses. Wood spirit and gasoline are often employed.

Acetic Acid HCO_2CH_3.—This is the sour substance in vinegar, and has many industrial applications. Vinegar is made by oxidizing alcohol with atmospheric oxygen, using an enzyme secreted by *bacterium aceti* (mother of vinegar) as contact agent. Dilute alcohol from any source, such as fermented apple juice (hard cider), is allowed to trickle over shavings in a barrel. Holes admit air, and the shavings are inoculated in advance by wetting with vinegar:

$$HOC_2H_5 + O_2 \rightarrow HCO_2CH_3 + H_2O.$$

The issuing liquid contains 5–15 per cent of acetic acid, which can be purified by fractional distillation to separate the water. It boils at 118° and freezes at 16.7°. Although four atoms of hydrogen are contained in its molecule, but one of these is replaceable by metals. This fact is recognized in the reaction formula (p. 95) of the acid, $HC_2H_3O_2$, or HCO_2CH_3. It is a weak, monobasic acid: $HCO_2CH_3 \rightleftarrows H^+ + CO_2CH_3^-$.

Destructive Distillation of Wood. Charcoal. — Dry wood is distilled in iron retorts, and the vapors coming off are led through a condenser to separate the liquids from the gases. The cellulose, lignin, and resinous material are decomposed, and only charcoal remains. The gases, consisting mainly of hydrogen, methane CH_4, ethane C_2H_6, ethylene C_2H_4, and carbon monoxide CO, are employed, on account of their combustibility, as fuel in the distillation itself. The fluids form a complex mixture containing large quantities of water, methyl alcohol CH_3OH (wood spirit), acetic acid, acetone $(CH_3)_2CO$, and tar. The liquids can be separated. The methyl alcohol (wood spirit) is used in varnish making. The acetone has several uses (*e.g.*, p. 394).

Wood **charcoal** exhibits the cellular structure of the material from which it was made, and is therefore highly porous and has an enormous internal *surface*. When the charcoal is burned, the mineral constituents of the wood appear in the ash. This is composed of the carbonates of the metallic elements present. For certain purposes, charcoals, made in the same fashion as the above from bones and from blood, find wide application. The former, called **bone black,** contains much calcium phosphate (p. 362). In the old method of making charcoal, which is still practised, the wood was piled up, covered with turf, and set on fire. All the valuable volatile products were lost, as well as part of the charcoal itself.

Properties of Charcoal. — Charcoal exhibits certain properties which are not shared by other forms of carbon. For example, it can take up large quantities of many gases. Boxwood charcoal will in this way absorb ninety times its own volume of ammonia, fifty-five volumes of hydrogen sulphide or nine volumes of oxygen. Freshly made dogwood charcoal (used in making the best gunpowder), when pulverized immediately after its preparation, often catches fire spontaneously on account of the heat liberated by the condensation of oxygen. It is therefore set aside for two weeks, to permit the slow absorption of moisture and air. The absorbed gases may be removed unchanged by heating the charcoal in a vacuum. The phenomenon, described as **adsorption,** is caused by the *ad*hesion of the gases to the very extensive surface (due to porosity) which the charcoal possesses. Glass and all other solids show the same property, though in a smaller degree (p. 88). Solid and liquid bodies are also in many cases taken up by charcoal in a similar fashion. Thus, organic dyes, such as indigo, litmus, and cochineal, and natural coloring matters (see sugar refining, p. 405), which are all more or less colloidal in nature, are removed when the liquid is shaken with, or poured through pulverized charcoal. The organic materials dissolved in drinking water also undergo adsorption in charcoal, but the charcoal soon becomes inactive. Charcoal is likewise used in reducing ores, and as a smokeless fuel.

Coal. — When vegetable matter decomposes, *without heating*, and while covered with sand or clay so that *air is excluded*, water and hydrocarbons are liberated, and the products are peat, bituminous coal, or anthracite.

We are concerned mainly with the products obtained by distilling coal, to get coal gas and coke, and with its use as fuel. To determine its suitability for various purposes, the coal is analyzed, and its heating power is measured.

In **coal analysis**, the air-dried material is used. The *water* is determined by heating 1 g. at 105° for 1 hour. Much water lowers the fuel value, because heat is wasted in vaporizing it, and in decomposing it (*cf.* p. 386). After reweighing the sample, the coal is heated with the Bunsen flame in a covered crucible to drive off the *volatile matter*. After weighing again, air is admitted, and strong heat is applied to burn up the *fixed carbon* (coke). The residue is the *ash*. In the following table the proportions are compared with seasoned wood on the one hand, and with charcoal and coke on the other.

The **calorific power** of a coal determines largely its value for heating. A sample (about 1 g.) is burned in a bomb calorimeter (p. 174). The rise in temperature of a known weight of surrounding water gives the number of calories. The coal is set on fire by a wire heated electrically. Engineers use the number of British Thermal Units (1 B.T.U. = heat required to raise 1 lb. of water 1° F.) developed by 1 pound of coal. The number of B.T.U. = 1.8 × number of calories per gram of coal. Bituminous coals give much, and widely varying amounts of volatile matter, while anthracite gives very little. The ash is the mineral

	Water.	Volatile matter.	Fixed carbon.	Ash.	Sulphur.	Cal. per 1 g.
Wood	20.0	49.0	30.0	1.0	....	3,100
Peat	20.0	51.6	25.0	3.2	0.2	4,270
Bituminous	1.3	36.7	53.5	8.5	1.7	7,800
Semi-bituminous	4.0	16.0	68.5	11	0.5	7,510
Anthracite	3.0	5.6	80.5	10.9	0.8	8,000
Charcoal	3.2	4.2	90.7	1.7	....	7,580
Coke	2.5	1.3	86.3	12.4	1.3	7,770
Petroleum	....	....	....	....	....	11,000

matter of the original plants, with rock material in many specimens. For coal gas, and even for coke, a coal high in volatile matter is chosen. For water gas (p. 386) anthracite or coke is employed.

If the heat of combustion of a coal is known, the amount of steam it should furnish can be calculated. It takes 100 cal. to raise 1 g. of water from 0° C. to 100° C. and 540 cal. more to convert it into steam. If the quantity of steam is too small, the furnace, draft, or firing is defective. Too much draft, for example, merely adds additional, useless air to be heated. If the flue gas, when analyzed, contains only 3 per cent of carbon dioxide, instead of the normal 12 per cent, then for every ton of coal burned, 52 tons of unnecessary air were raised to the temperature of the furnace. Tests of this kind can control the efficiency of every device in a modern factory, and they ought to be in universal use.

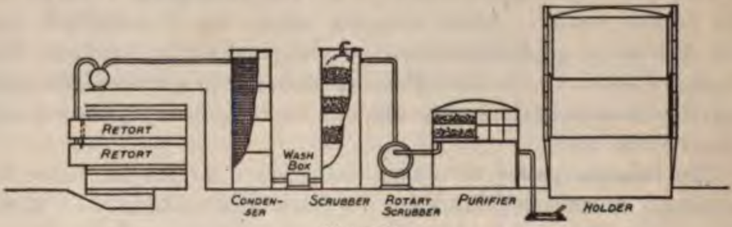


FIG. 110.

Coal Gas. — The gas plant (Fig. 110) includes: (1) The firebrick retorts in which the coal is heated to 1300°, (2) the hydraulic main, a wide iron pipe above them in which the tar collects, (3) the condenser and wash box for cooling and condensing oils, (4) the scrubbers where the ammonia is taken out by water, (5) the purifier where hydrogen sulphide is absorbed by hydrated ferric oxide and (6) the holder where the gas collects.

One short ton (2000 lbs.) of the bituminous coal in the above table gave: Gas 10,500 cu. ft. with 13 candle power, coke 1325 lbs., ammonia 5 lbs. (= 20 lbs. $(NH_4)_2SO_4$ worth $60 per ton), and tar 12 gallons. The components of the gas were: Illuminants 3.8, heating gases 90.2, impurities 6.0. Calorific power of gas 610 B.T.U. per cu. ft.; sp. gr. (air = 1) 0.43.

The tar is frequently distilled fractionally and yields: Benzene C_6H_6, from which aniline and many dyes and drugs are prepared; naphthalene $C_{10}H_8$, sold as moth-balls, and the starting point for synthetic indigo; anthracene $C_{14}H_{10}$, from which valuable dyes such as alizarin and indanthrene are made; phenol or carbolic acid (p. 349), and other useful substances. A rougher separation yields tar and pitch, for road-making, preserving timber, and waterproofing roofs.

Coke. — The **beehive** coke oven is a brick structure shaped like a beehive, with an additional opening at the top. The coal which fills it burns with a limited supply of air. All the vapors and gas burn at the upper opening, and the ammonia and tar and combustible gas are therefore wasted (*cf.* p. 340).

The **by-product coke oven** is a good deal like a gas plant. The chief difference is that the heating is arranged so as to decompose as much of the volatile matter as possible, and cause it to leave its carbon in the retort. The gas is therefore poor in illuminants, but excellent as fuel. The ammonia and tar are diminished in amount, but still valuable products. The yield of coke is about 73 per cent of the original coal, against 66 per cent from the beehive oven.

Burning coke gives a higher temperature than does coal, because no heat is used in vaporizing moisture and volatile matter. For the same reason, it burns without flame. Because of these and other properties, it is employed in immense quantities in reducing ores of iron in the blast furnace, as well as for many other purposes.

CHAPTER XXXI

ORGANIC ACIDS AND SALTS. ALCOHOLS, ESTERS. FOODS

THUS far, one acid, acetic acid, and two alcohols, methyl and ethyl alcohol, have been mentioned. But there are whole series of organic acids, corresponding to the series of hydrocarbons.

Organic Acids and Their Salts. — The general formula of the saturated series of **monobasic acids** is $H(CO_2C_nH_{2n+1})$. Thus:

Formic acid ($n = 0$), $H(CO_2H)$.
Acetic acid ($n = 1$), $H(CO_2CH_3)$.
Butyric acid ($n = 2$), $H(CO_2C_2H_5)$.
Palmitic acid ($n = 15$), $H(CO_2C_{15}H_{31})$.
Stearic acid ($n = 17$), $H(CO_2C_{17}H_{35})$.

Formic (Lat., *an ant*) acid is secreted by red ants, and is found in stinging nettles. Formic (b.-p. 100.1°), acetic, and butyric acids are liquids. Palmitic and stearic acids are solids, and are mixed with paraffin in making candles.

Acids containing relatively less hydrogen are unsaturated. Thus, oleic acid ($n = 17$) is $H(CO_2C_{17}H_{33})$.

The acids with large molecular weight are insoluble in water. All the acids, however, react with sodium hydroxide solution, giving soluble salts. Thus, palmitic acid gives sodium palmitate:

$$NaOH + H(CO_2C_{15}H_{31}) \rightleftarrows H_2O + Na(CO_2C_{15}H_{31}).$$

Other salts are sodium formate (p. 385) $Na(CO_2H)$, sodium acetate $Na(CO_2CH_3)$, sodium stearate $Na(CO_2C_{17}H_{35})$, sodium oleate $Na(CO_2C_{17}H_{33})$. Common *soap* is a mixture of the last two salts with sodium palmitate.

Later, in discussing fats and soap, it will be convenient to abbreviate the formulæ. A monobasic acid will be indicated by the formula HCO_2R and a salt by $NaCO_2R$ or $Ca(CO_2R)_2$, where R stands for a hydrocarbon radical or group of atoms, such as C_nH_{2n+1}. In organic chemistry a radical is *not* always able to form an ion. Here the ion is CO_2R^-.

There are also **dibasic acids.** **Oxalic acid** (p. 385) $H_2C_2O_4$ is the simplest of these. It may be made by the oxidation of sugar with nitric acid. The white crystals used in the laboratory are the hydrate $H_2C_2O_4,2H_2O$.

Alcohols. — Methyl alcohol CH_3OH (p. 408) and ethyl alcohol C_2H_5OH (p. 406) are the first two members of the series $C_nH_{2n+1}OH$. There are also many alcohols with more than one OH group in each molecule. Of these, the one we shall presently encounter is **glycerine** $C_3H_5(OH)_3$. The sugars are alcohols with several hydroxyl radicals.

Esters. — When an acid and an alcohol are mixed, an **ester** and water are formed. The action is slow and, being reversible, is always incomplete. But, by introduction of a dehydrating agent, like concentrated sulphuric acid, the water is removed and the change brought to completion. Thus, ethyl alcohol and acetic acid, when warmed with sulphuric acid, give **ethyl acetate:**

$$C_2H_5OH + HCO_2CH_3 \rightleftarrows C_2H_5CO_2CH_3 + H_2O.$$

This action has the appearance of a neutralization (p. 256), but is different in several ways. Alcohol is not a base, and in aqueous solution it does not conduct electricity. Then, true neutralization takes place instantly, while the foregoing action, and all like it, proceed very slowly. Thus, although acetic acid is a true acid, it is not *here* interacting with a base.

With the assistance of a dehydrating agent, similar actions take place between any alcohol and any acid (organic or inorganic). The action of cellulose or of glycerine with nitric acid (p. 350) is such an interaction. Again, for example:

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{acetic acid}}{3H(CO_2CH_3)} \rightleftarrows \underset{\text{glyceryl acetate}}{C_3H_5(CO_2CH_3)_3} + 3H_2O,$$

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{stearic acid}}{3H(CO_2C_{17}H_{35})} \rightleftarrows \underset{\text{glyceryl stearate}}{C_3H_5(CO_2C_{17}H_{35})_3} + 3H_2O.$$

The glyceryl radical $C_3H_5^{III}$ is trivalent, and takes the place of three atoms of hydrogen. The products are named as if they were salts, but they are not ionized in solution and do not react with acids, bases, salts, by instantaneous double decomposition, as do true salts. To distinguish them from salts, they are called **esters** — $R'(CO_2R)$.

Fats and Animal and Vegetable Oils. — The fats and oils found in animal tissue, or pressed from seeds of plants, are composed mainly of esters. Beef **fat** is a mixture of about three-fourths glyceryl palmitate (palmitin) $C_3H_5(CO_2C_{15}H_{31})_3$ and glyceryl stearate (stearin) $C_3H_5(CO_2C_{17}H_{35})_3$, along with one-fourth glyceryl oleate (olein) $C_3H_5(CO_2C_{17}H_{33})_3$. **Lard** (hog fat) contains a much larger proportion of the last (60 per cent) and is therefore softer. **Butter** contains the same esters, along with some water and some glyceryl butyrate (butyrin) $C_3H_5(CO_2C_3H_7)_3$. **Olive oil** contains much olein (75 per cent). **Cottonseed oil** is similar in composition, and is used as a substitute for olive oil, or for butter in cooking.

All these fats and oils contain a certain proportion of the *free organic acids* (see p. 420). These oils must not be confused with mineral oils, which are mixtures of hydrocarbons.

As regards **physical properties,** these oils are all insoluble in water, and the heavier ones also in cold alcohol. They dissolve readily, however, in ether, benzene, carbon disulphide, and carbon tetrachloride. Hence, benzene is used in dry cleaning clothing made of silk or wool. The two last solvents are used in extracting vegetable oils.

Chemical Properties of Fats and Oils. — All fats and oils, when boiled with water, and more rapidly when heated (200°) with water in a closed vessel, are decomposed. The ester is hydrolyzed, and the actions in the three equations last given (p. 413) are reversed. Thus, with stearin:

$$\underset{\text{stearin}}{C_3H_5(CO_2C_{17}H_{35})_3} + 3H_2O \rightarrow \underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{stearic acid}}{3HCO_2C_{17}H_{35}},$$

and when the mixture is cooled, the acid, being insoluble in water, forms a solid cake while the glycerine is in solution in the water. If a mixture like beef fat is heated with water in this way, a mixture of palmitic, stearic, and oleic acids is obtained. The oleic acid (liquid) is pressed out, and the residue is mixed with paraffin to make candles. The glycerine is separated from the water and used in making nitroglycerine (glyceryl nitrate, an ester) and in medicine.

When the fat is heated with aqueous sodium hydroxide, the soluble sodium salts of the acids are formed. Since these salts are known as soaps, this action of a base on an ester is called **saponification:**

$$\underset{\text{stearin}}{C_3H_5(CO_2C_{17}H_{35})_3} + 3NaOH \rightarrow \underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\substack{\text{sodium stearate}\\ \text{(a soap)}}}{3Na(CO_2C_{17}H_{35})}.$$

When common salt is added to the solution ("salting out"), the sodium salts of the three acids (the soap) are coagulated and separated as a floating layer, which solidifies when cold. The glycerine is contained in the salt solution.

With potassium hydroxide, the potassium salts are obtained, and constitute **soft soap.**

The soaps are purified by redissolving and again salting out. Dyes and perfumes are often added. Floating varieties are made by beating the soap before it solidifies, and so introducing bubbles of air. Fine sand or pumice is added to make scouring soaps. Mixing with glycerine or sugar gives transparent soap.

Chemical Properties of Soaps. — Since the soaps are soluble salts of sodium, they are largely ionized in solution and interact with acids by double decomposition:

$$Na(CO_2C_{17}H_{35}) + HCl \rightarrow NaCl + H(CO_2C_{17}H_{35})\downarrow.$$

The acids, being insoluble, are precipitated. They also enter into double decomposition with other salts. Thus, hard water, containing compounds of calcium and magnesium in solution, give precipitates of the corresponding salts. For example:

$$2Na(CO_2C_{17}H_{35}) + CaSO_4 \rightarrow Na_2SO_4 + Ca(CO_2C_{17}H_{35})_2\downarrow.$$

Thus, with hard water, much soap is wasted in precipitating the "hardness."

Colloidal Suspension. — To explain the cleansing power of soap, it is necessary to learn more about colloids, for soap in solution is essentially colloidal.

The simplest colloidal suspensions are those of metals like gold and platinum. They can be made by forming an electric arc between the points of two wires, while the points are immersed in water. Liquids of various colors, depending on the degree of **dispersion** (fineness of the particles) of the metal, are thus formed. Such a liquid (1) leaves no deposit on filter paper, (2) shows no elevation in the boiling-point of the solvent and (3) no depression in the freezing-point. (4) The suspended body has little or no tendency to diffuse into a layer of the pure solvent. In consequence, if the colloidal solution is placed in a diffusion-shell, which is a test-tube shaped tube of filter-paper or parchment, immersed in water, none of the colloid escapes through the pores of the shell. Ordinary solutes escape more or less quickly, according to their molecular weight. Hence, a diffusion shell can be used to *separate* a mixture of colloidal and non-colloidal material. Thus, salt, if present with colloidal starch, or sugar if present with colloidal gold, can be removed by changing the water round the shell until no more salt (or sugar) is found to come out. This process is called **dialysis**, and was devised by Graham.

(5) The most striking property of colloids is shown by the **ultramicroscope.** In a perfectly darkened room, a converging beam of strong light is sent horizontally through the liquid (Fig. 111) and the place where the light is focussed is viewed from above, through a microscope. Under such circumstances, a true solution remains perfectly dark, but a colloidal suspension shows minute points of light, first studied by Tyndall. Colloidal gold, solutions of soap, starch, gelatine and dyes, and many other liquids exhibit the phenomenon. The points of light, due to particles which, although minute, contain many molecules, show also a trembling or vibrating movement, first noticed by a botanist Brown (1827) and called the **Brownian Movement.** The motion is due to collisions of the moving molecules of the solvent with the suspended particles of the colloid and, when the suspension is very fine (highly "disperse"), the particles shoot about rapidly.

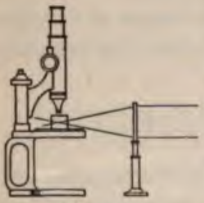


FIG. 111.

Other properties of colloidal suspensions are discussed below.

Theory of Colloidal Suspension and Coagulation. — When wires from a battery are immersed in the liquid, the particles of a colloid are found to move slowly either with or against the positive current. The phenomenon is called **electrophoresis.** Apparently, the colloidal particles are aggregates of molecules of an insoluble substance, collected round an ion. The particles, although relatively large in proportion to the charge, move almost as rapidly as in ionic migration (p. 231). This affords an explanation of the fact that the particles remain suspended, and do not settle. They are individually so small that they are kept in motion by collisions with the molecules of the solvent. If they could unite into large aggregates — like the particles of a precipitate — they would separate like any ordinary, insoluble substance. But, having like electrical charges, they *repel* one another, and so remain separate and in suspension.

Now those colloids which have distinct electrical charges can be **coagulated** or flocculated, and so precipitated in the liquid, by adding a solution of an ionized substance. Thus, colloidal gold and other metals are negative, and an equivalent amount of a positive ion, usually H^+, is present also. When a salt is added, the positive ion of the salt attaches itself to the negative colloidal metallic particles, neutral bodies result, coagulation can now occur, and precipitation follows. Bivalent ions are more effective than univalent ones (see arsenic trisulphide). Conversely, a positive colloid, like ferric hydroxide, is coagulated by the negative ion of the salt, and more easily the higher the valence of the negative ion. Furthermore, one colloid will coagulate another of opposite charge. Thus, metaphosphoric acid is a negative colloid when in solution, while ortho- and pyrophosphoric acid are not colloidal. Albumin is usually a positive colloid. Hence (p. 372), metaphosphoric acid and albumin coagulate and precipitate one another, while the other two acids have no action on albumin.

Starch and gelatine are neutral colloids, and are not easily coagulated.

Soap Solution Colloidal, Salting Out. — Soap solution, under the ultramicroscope, is seen to contain suspended particles. A test with litmus also shows that the soap is partly hydrolyzed:

$$Na(CO_2R) + H_2O \rightleftarrows H(CO_2R) + NaOH.$$

Being a salt of a little ionized acid, the negative ion of the soap tends to combine with the H^+ of the water: $H^+ + (CO_2R)^- \rightleftarrows H(CO_2R)$, leaving the ions of sodium hydroxide. Now the acid thus set free combines with the undissociated molecules of the salt to form an acid salt $NaH(CO_2R)_2$. This acid salt is insoluble, but remains in colloidal suspension as a negative colloid. When a strong solution of common salt (or even excess of sodium hydroxide) is added, the positive ion Na^+ is adsorbed by the negative colloid (the acid salt) and the latter is coagulated. In coming out as a precipitate, it seems to adsorb most of the sodium hydroxide, so that the precipitate has the composition of soap.

The Cleansing Power of Soap. Emulsions. — As a cleanser, soap solution — or suspension, as we should now call it — has two properties. It removes oil and grease (insoluble liquids) by forming an *emulsion* with them. It also removes minute solid particles of dirt, by taking the dirt into *suspension* (next section).

When an oil, such as kerosene, is violently shaken with water, both liquids are broken into minute droplets, and an opaque mixture results. The droplets of each liquid, however, quickly join together and soon the mass clears up and shows the two liquids in separate layers. If, however, a colloidal suspension is used, instead of pure water, the droplets unite much more slowly, if at all, and a more or less permanent, opaque, rather viscous mass results. Such a mixture of two mutually insoluble liquids is called an **emulsion.** Thus, a few drops of soap solution will cause the kerosene and water to remain much longer in the condition of an emulsion. Similarly, vinegar and olive oil, when vigorously beaten (French dressing) separate rather quickly into two layers. But if the yolk of an egg (colloidal) is added to the vinegar, a stiff, almost solid mass can be made (Mayonnaise dressing) which will remain permanently emulsified. In removing grease, therefore, *rubbing* with soap solution turns the grease into suspended droplets (emulsifies it), and so the grease can be washed away.

This behavior of a colloid can be **explained.** When the kerosene and water are divided into droplets, with a great increase in the total surface, and in the surface energy of both, the surface tension of water, which is great, favors the reunion of the drops, with diminishing surface, and dissipation of the surface energy. Now, while *ordinary*, dilute solutions have a surface tension close to that of water, colloidal solutions (such as 0.5 per cent soap solution) have a very low surface tension. Hence, the tendency to diminish the surface of droplets of soap solution, by coalescence, is slight and ineffective. Furthermore, as predicted by Willard Gibbs of Yale University, and proved by experiment, a colloid has the peculiarity that it tends to reach a higher concentration in the surface layer than it has elsewhere in the liquid. When the colloid has adjusted itself to a state of *equilibrium*, in this regard, *it resists a decrease in the surface* (which would *increase* its concentration beyond the equilibrium value), just as much as it resists an increase, which would *diminish* its concentration. The emulsion of a colloidal suspension with an immiscible liquid is thus a stable condition.

Experiments confirming this view are easily made. If a solution of a dye like methyl violet (colloid) be shaken violently, and the froth (large surface in proportion to quantity of liquid) be separated, it is found that the liquid produced by the subsidence of the froth (an emulsion with *air* is not permanent), is darker in shade, and contains more dye, than an equal amount of the original liquid. Soap solution, after being shaken likewise, contains relatively more soap in the froth than in the liquid.

Adsorption of Colloidal Matter. — As we have seen (p. 409), when liquids containing colloidal substances, such as dyes and natural organic coloring matters, are shaken with pulverized charcoal, the colloid is **adsorbed** by the charcoal — that is, it adheres to the surface of the particles of the charcoal. This principle is used in decolorizing sugar (p. 405) and in "bleaching" oils. Now, soap is also removed by shaking with charcoal or with infusorial earth, in the same fashion.

Pulverized charcoal is, relatively, a coarse powder. If soot, which is very finely divided carbon, be freed from oil or grease by washing with ether, it gives a loose, non-caking powder. If this powder be shaken with water, it settles. If it be shaken with dilute soap solution, it remains in suspension, and the liquid resembles ink. The particles are so fine that, instead of carrying down the colloidal soap, and forming a precipitate, as charcoal does, they attach themselves to the colloidal soap, and remain suspended. This is therefore adsorption, with the difference from the ordinary phenomenon, that the colloid carries off the adsorbent, instead of the adsorbent carrying down the colloid. Now dirt is composed largely of soot, and equally fine particles of other substances. Hence, the soap first emulsifies the oil on the hands (or on soiled linen, for example) and then adsorbs the particles of dirt which are thus set free.

Formerly, soap solution was supposed to remove grease (and soot?) because of its slight alkaline reaction, due to hydrolysis. This explanation must be given up, because: (1) an alkali so dilute that it exists in equilibrium with the free fatty acid, can not possibly saponify the *ester* contained in a grease spot. (2) Pure alkali of the same concentration (or stronger) has no more emulsifying power than has water. Such an alkaline solution will indeed emulsify an animal or vegetable oil (cod-liver oil, cotton oil, castor oil), but it does so by interacting with the free fatty acid always present in such oil (p. 414) and *forming therefrom a soap.* Such an alkaline solution does *not* emulsify kerosene, although soap solution does. The emulsifying agency in each case is a soap. (3) Very dilute alkali has no more effect upon soot than has water, — but soap solution takes clean (greaseless) soot instantly into permanent suspension. (4) An aqueous solution of saponin $C_{32}H_{54}O_{18}$, obtainable from several plants, although it contains no alkali, lathers, emulsifies, and adsorbs dirt, just as does soap. It is a colloid.

CYANOGEN

Cyanogen C_2N_2. — This compound is prepared by allowing a solution of cupric sulphate to trickle into a warm solution of potassium cyanide. The cupric cyanide, at first precipitated, quickly decomposes, giving cuprous cyanide and cyanogen:

$$2KNC + CuSO_4 \rightarrow Cu(NC)_2\downarrow + K_2SO_4,$$
$$2Cu(NC)_2 \rightarrow 2CuNC + C_2N_2\uparrow.$$

Cyanogen is a very poisonous gas with a characteristic, faint odor.

Hydrocyanic Acid HNC. — This acid, called also **prussic acid,** is most easily made by the action of an acid upon a cyanide (see Potassium cyanide), followed by distillation. It is a colorless liquid boiling at 26.5°. It has an odor like that of bitter almonds, and is highly poisonous. In aqueous solution it is an extremely feeble acid. Hydrocyanic acid and the cyanides are unsaturated compounds, a fact which is illustrated in the two following paragraphs.

Cyanates and Thiocyanates. — When potassium cyanide is fused and stirred with an easily reducible oxide, like lead oxide (PbO), the metal (for example, the lead) collects at the bottom of the iron crucible in molten form, and **potassium cyanate** $KNCO$ is produced:

$$KNC + PbO \rightarrow KNCO + Pb.$$

Ammonium cyanate NH_4NCO, when dissolved in warm water, undergoes a profound change. It turns into **urea** $(NH_2)_2CO$ (carbamide), which has the *same composition*. The former is a salt, and is ionized, and enters into double decompositions: the latter is not ionized, but is like ammonia, able to combine with acids. This is an example of **internal rearrangement** (p. 148). Two substances, of the same composition and molecular weight, but different chemical behavior, are called **isomers**. Urea is one of the forms in which nitrogen is eliminated by animals. The preparation of what seemed to be a typical product of life from a substance (ammonium cyanate) easily made, if necessary, from the four elements themselves, was the first case of the artificial production of an organic compound, and created a great sensation when it was first accomplished by Wöhler in 1828.

When potassium cyanide in aqueous solution is boiled with sulphur or with a polysulphide (p. 274), it is converted into **potassium thiocyanate** $KCNS$. This salt, or **ammonium thiocyanate** NH_4CNS, is used in testing for ferric ions on account of the deep-red color of ferric thiocyanate (*cf.* p. 182).

FOODS

Plants and animals contain substances which are similar in composition, such as sucrose and lactose (p. 404), starch and glycogen $(C_6H_{10}O_5)_x$, animal fats and vegetable oils (both esters). Albumins and other proteins are found in both. They differ, however, markedly in the sources of these substances. The plant uses simple materials, like carbon dioxide, water, and potassium nitrate. The animal can make no use of these substances — it must be fed on complex compounds of animal or vegetable origin.

Foods. — Since the animal is continuously eliminating carbon dioxide, moisture, compounds of nitrogen, salts, and other substances, and is also giving off heat, these materials must be replaced, and fuel must be furnished. Like the plant, an animal can absorb only dissolved material. But it prepares its own solutions in a remarkable laboratory, the *digestive tract*. The production of suitable soluble substances is called *digestion*.

The table shows the chief components of animal food, and the proportion in which each is present in the chief foods used by man:

	Water.	Protein.	Fat.	Carbohydrate.	Ash.
Beef (lean)	73.8	22.1	2.9	....	1.2
Cod	82.6	15.8	0.4	....	1.2
Eggs	73.7	14.8	10.5	....	1.0
Milk *	87.0	3.3	4.0	5.0	0.7
Butter	11.0	1.0	85.0	....	3.0
Cheese (cheddar)	27.4	27.7	36.8	4.1	4.0
Oatmeal	7.3	16.1	7.2	67.5	1.9
Wheat flour	11.9	13.3	1.5	72.7	0.6
Beans (dried)	12.6	22.5	1.8	59.6	3.5
Almonds	4.8	21.0	54.9	17.3	2.0
Maize (green corn)	75.4	3.1	1.1	19.7	0.7
Potatoes	78.3	2.2	0.1	18.4	1.0
Lettuce	94.7	1.2	0.3	2.9	0.9

* The emulsified fat separates slowly as the cream; the protein (casein, colloidally suspended in the skim milk) is coagulated by rennet and constitutes cheese; the carbohydrates (lactose, a sugar) is then left in the water, along with inorganic salts.

We observe that the common animal foods, except milk, containing lactose (p. 404), carry no carbohydrates (the ox liver contains about 2 per cent of glycogen); that potatoes and corn, when dried, are nearly all starch; that lean meat, dry, is all protein; that some seeds (wheat and beans) contain little fat, some (oats) much more fat, and some (almonds and nuts) a large amount; and that lettuce is mainly water, with useful inorganic salts in solution, and cellulose.

The **proteins**, several of which have been mentioned (pp. 312, 340, 359) are white, amorphous substances containing, besides carbon, hydrogen, and oxygen, a large proportion of nitrogen (16 per cent), some sulphur (1 per cent) and frequently iron and phosphorus as well.

Digestion. — The process of rendering the constituents of food soluble is like fermentation (p. 406) — it is performed mainly by enzymes. Each class of components is handled by one or more enzymes. Thus, **starch** (in bread and potatoes) is partly digested during mastication by ptyalin (an amylase, p. 406) in the saliva, and partly by amylopsin in the small intestine. The resulting maltose is decomposed into glucose by another enzyme, and passes into the blood where it is oxidized, furnishing heat. In diabetes, much of the glucose escapes oxidation, and is eliminated. Again, the **fats** are hydrolyzed into the acids and glycerine by lipases (fat-splitting enzymes) in the bile, and the acids go into solution (probably colloidal). The acids and glycerine recombine to form fats in the blood, and are either deposited in the tissues or oxidized. Finally, the **proteins** are changed in a similar way into peptones which are soluble in water, and in this form are able to pass through the wall of the intestine.

Fuel Value of Food. — Although food is required to replace waste, much of it is needed to furnish energy, by its oxidation, so that muscular movements may be maintained, and the temperature of the body kept up to its normal value (37° C.). Thus, the **fuel values** of foods are important. The average fuel values, expressed in *large calories* (1 Cal. = 1000 cal. as previously defined, p. 174), per gram, are:

Carbohydrates, 4 Cal. Fats, 9 Cal. Proteins, 4 Cal.

The fuel values *per pound* (453.6 g.) are 453.6 times greater.

Healthy life cannot be maintained on one kind of food — a mixed diet is necessary. In general, it is held that 100 g. of proteins (giving 400 Cal.) per day, and a sufficient amount of other foods to give a total fuel value of 2200 cal. is enough for a person doing no physical labor. When physical labor is involved, larger values, up to 3800 cal. per day, are necessary. The data in the table (p. 422) will enable one to calculate the fuel value of 100 g. (or of 1 lb.) of each kind of food.

Exercises. — 1. Make the graphic formulæ of ethyl formate, ethylene bromide (p. 393), ethyl alcohol.

2. Make equations for the formation of palmitin (p. 413), the saponification of olein (p. 415).

3. Prepare a **summary** of the various statements that have been made in the text about **catalysis** (*e.g.*, pp. 29, 59, 156, 160, 279, 288, 341, 361, 406), and illustrate fully.

4. Calculate the fuel value of 1 lb. each of (*a*) oatmeal, (*b*) potatoes, (*c*) lettuce.

5. Calculate the weights, both in pounds and in grams, of 100 Cal. portions of (*a*) eggs, (*b*) wheat flour, (*c*) almonds, (*d*) lettuce.

6. At current market prices, what would be the cost per 100 Cal. portion of beef, cod, butter, and wheat flour, respectively.

CHAPTER XXXII

SILICON AND BORON

IN respect to **chemical relations** there is a close resemblance between silicon and carbon. Silicon gives a monoxide, but is quadrivalent in all its other compounds. It is a non-metallic element.

Occurrence. — Silicon, unlike carbon, is not found in the free condition. In combination it is the most plentiful element after oxygen, and constitutes more than one-quarter of the crust of the earth. The oxide is silica or sand (SiO_2), and this oxide and its compounds are components of many rocks. In the inorganic world silicon is the characteristic element to almost as great an extent as is carbon in the organic realm.

Preparation of Silicon. — When finely powdered magnesium and sand are mixed, and one part of the mass is heated, a violent action spreads rapidly through the whole:

$$2Mg + SiO_2 \rightarrow Si + 2MgO.$$

At the same time, and especially if excess of the metal is used, some magnesium silicide Mg_2Si is formed also. The mixture is treated with a dilute acid which decomposes the magnesium oxide and the silicide (see below), and leaves the **silicon** (**amorphous**) undissolved. When amorphous silicon is dissolved in molten zinc, the mass, when solid, contains **crystalline silicon.** The zinc is removed by the action of a dilute acid, the silicon remaining unaffected.

Silicon and **ferrosilicon** (an alloy of iron and silicon) are now made on a large scale, the former by heating sand and carbon, the latter by heating a mixture of ferric oxide and sand with carbon in the electric furnace (p. 377).

Properties. — **Amorphous silicon** is a brown powder. It unites with fluorine at the ordinary temperature, with chlorine at

430°, with bromine at 500°, with oxygen at 400°, with sulphur at 600°, with nitrogen at about 1000°, and with carbon and boron at temperatures attainable only in the electric furnace. It is dissolved by a mixture of hydrofluoric acid and nitric acid, giving silicon tetrafluoride. **Crystallized silicon** forms black needles belonging to the hexagonal system. Silicon and ferrosilicon act readily upon a cold solution of sodium hydroxide (*cf.* p. 56), the ortho- or metasilicate of sodium being formed:

$$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2\uparrow.$$

This is one of the sources of hydrogen for filling balloons and airships.

Silicon Hydride SiH_4. — Silicon differs from carbon in giving only two well-defined compounds with hydrogen. The chief one may be liberated as a gas by the action of hydrochloric acid upon magnesium silicide:

$$Mg_2Si + 4HCl \rightarrow 2MgCl_2 + SiH_4.$$

The action is like that by which hydrogen sulphide is made. The gas is easily inflammable, and burns to form water and silicon dioxide. When heated alone, it decomposes into its constituents.

Silicon Tetrachloride and Tetrafluoride. — The tetrachloride $SiCl_4$ is formed by direct union of the free elements. It may also be prepared by passing chlorine over a strongly heated mixture of silicon dioxide and carbon. The products enter a condenser in which the tetrachloride assumes the liquid form:

$$2Cl_2 + SiO_2 + 2C \rightarrow SiCl_4 + 2CO.$$

Chlorine is unable to displace oxygen from combination with silicon, and has, therefore, when alone, no effect upon sand. In the above action, therefore, the carbon is used to secure the oxygen while the chlorine combines with the silicon. This kind of interaction was formerly used for making many chlorides (*e.g.*, BCl_3, $AlCl_3$, $CrCl_3$) from oxides, before simple ways of obtaining the elements in the free condition were known.

Silicon tetrachloride is a colorless liquid (b.-p. 59°), which fumes strongly in moist air, and with water precipitates silicic acid:

$$SiCl_4 + 4H_2O \rightarrow 4HCl + Si(OH)_4\downarrow.$$

When strong hydrofluoric acid acts upon sand, **silicon tetrafluoride** SiF_4 is liberated:

$$SiO_2 + 4HF \rightarrow 2H_2O + SiF_4.$$

Since the water interacts with the tetrafluoride (see below), the latter is usually made by heating sand with powdered calcium fluoride and excess of sulphuric acid. In this way the hydrogen fluoride is generated in contact with the sand, and at the same time the sulphuric acid renders the water inactive. Hydrofluoric acid acts in a corresponding way upon all silicates (*q.v.*), whether these are minerals or are artificial silicates like glass (*cf.* p. 206).

Silicon tetrafluoride is a colorless gas. It fumes strongly in moist air, and acts vigorously upon water. This interaction is different from that of the tetrachloride, because the excess of the tetrafluoride forms a complex compound with the hydrofluoric acid:

$$\begin{array}{ll} SiF_4 + 4H_2O \rightarrow Si(OH)_4\ (+\ 4HF). & (1) \\ \underline{(4HF) + 2SiF_4 \rightarrow 2H_2SiF_6.\qquad\qquad} & (2) \\ 3SiF_4 + 4H_2O \rightarrow Si(OH)_4 + 2H_2SiF_6. & \end{array}$$

The silicic acid is precipitated in the water, and may be separated by filtration, leaving a solution of **hydrofluosilicic acid.**

Hydrofluosilicic Acid H_2SiF_6. — This acid is stable only in solution. When the water is removed by evaporation, silicon tetrafluoride is given off, while most of the hydrogen fluoride remains to the last. Its salts are decomposed in a corresponding way when they are heated. This acid is used in analysis chiefly because its potassium salt K_2SiF_6 is one of the few salts of this metal which are relatively insoluble in water. The barium salt is also insoluble, but most of the salts of the heavy metals are soluble.

Silicon Dioxide SiO_2. — This substance is found in many different forms in nature. In large, transparent, six-sided prisms with pyramidal ends it is known as **quartz** or **rock crystal.** When colored by manganese and iron it is called **amethyst,** when by organic matter, **smoky quartz.** A special arrangement of the structure gives **cat's eye.** Amorphous forms of the same material, often colored brown or red with ferric oxide, are **agate, jasper,** and **onyx,** the last much used in making cameos. Slightly hydrated varieties of silica are the **opal** and **flint.** Forms produced by organisms are **sponges** and **infusorial earth** (**Tripoli**). The latter is used in scouring materials and for decolorizing oils (p. 419).

Silica is found in the hard parts of straw, of some species of horsetail (*equisetum*), and of bamboo. In the form of whetstones it is used for grinding. The clear crystals are employed in making spectacles and optical instruments and are more transparent to ultra-violet light than is glass. Pure sand is used in glass manufacture (*q.v.*). Recently, small pieces of chemical apparatus have been manufactured by fusing quartz (m.-p. 1600°) in the oxy-hydrogen flame or the electric furnace. The material does not crystallize on cooling, and is amorphous, like glass. Owing to the low coefficient of expansion of silica, the vessels can be heated red hot and chilled in cold water without risk of fracture.

Silicates. Water Glass. — Silicon dioxide, although differing profoundly from carbon dioxide in its physical nature, nevertheless behaves like the latter chemically. Thus, when boiled with sodium hydroxide solution it forms sodium metasilicate Na_2SiO_3 or orthosilicate Na_4SiO_4.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O.$$

The salt is left as a gelatinous solid ("soluble glass") when the water is evaporated. The silicates of potassium and sodium may also be obtained by boiling sand with the carbonates of these metals, or, more rapidly, usually as metasilicates (see below), by *fusing* the mixture:

$$SiO_2 + K_2CO_3 \rightarrow K_2SiO_3 + CO_2\uparrow .$$

Water glass or soluble glass, being a salt of a feeble acid with an active base, gives a solution with an alkaline reaction (p. 271, 383). When manufactured for commercial use, it has the composition $Na_2Si_2O_5(Na_2SiO_3,SiO_2)$, and gives a less alkaline solution. It is used as a filler in cheap soaps, for fireproofing and waterproofing timber and textiles, and for preserving eggs.

Silicic Acid H_4SiO_4. — When acids are added to a solution of sodium silicate, silicic acid is set free. After a little delay it usually appears as a gelatinous precipitate. When, however, the silicate is poured into excess of hydrochloric acid, no precipitation occurs. The silicic acid remains in **colloidal suspension.** The acid is ortho-silicic acid:

$$Na_4SiO_4 + 4HCl \rightarrow 4NaCl + H_4SiO_4\downarrow,$$
$$Na_2SiO_3 + 2HCl + H_2O \rightarrow 2NaCl + H_4SiO_4\downarrow,$$

but the gelatinous precipitate, when dried, loses the elements of water. There seem to be no definite stages, indicating the existence of various acids, such as we observe with phosphoric acid. The final product of drying is the dioxide. Silicic acid is a very feeble acid and, therefore, gives no salt with ammonium hydroxide (feeble base).

The suspension of colloidal silicic acid can be freed from the acid and sodium chloride (see equation, above) by dialysis (p. 416). It is a positive or a negative colloid, according to the mode of preparation, and the two kinds are coagulated by addition of salts having bivalent negative and positive ions, respectively.

Mineral Silicates. — While silicic acid is the ortho-acid H_4SiO_4, and no other silicic acids have been made, the salts are most easily classified by imagining them to be derived from various acids representing different degrees of hydration of the dioxide (*cf.* p. 369), or, to put it the other way, different degrees of dehydration of the ortho-acid. The following equations show the relation of the ortho-acid to some of the silicic acids whose salts are most commonly found amongst minerals:

$$\begin{array}{ll} H_4SiO_4 - H_2O \rightarrow H_2SiO_3\ (= H_2O,SiO_2) & \text{Metasilicic acid.} \\ \left.\begin{array}{l} 2H_4SiO_4 - H_2O \rightarrow H_6Si_2O_7\ (= 3H_2O,2SiO_2) \\ 2H_4SiO_4 - 3H_2O \rightarrow H_2Si_2O_5\ (= H_2O,2SiO_2) \end{array}\right\} & \text{Disilicic acids.} \\ 3H_4SiO_4 - 4H_2O \rightarrow H_4Si_3O_8\ (= 2H_2O,3SiO_2) & \text{Trisilicic acid.} \end{array}$$

Di- and trisilicates are those derived from acids containing two and three units of silicic anhydride, respectively, in the formula. The valences of the negative radicals of the acids are shown by the number of hydrogen units in the formulæ.

The composition of minerals is often exceedingly complex. This is due to the fact that amongst them mixed salts (p. 245) are very common, in which the hydrogen of the imaginary acid is displaced by two or more metals in such a way that the total quantity of the metals is equivalent to the hydrogen. The following list presents in tabular form some **typical or common minerals** arranged according to the foregoing classification:

ORTHOSILICATES (H_4SiO_4)
- Zircon, $ZrSiO_4$
- Garnet, $Ca_3Al_2(SiO_4)_3$
- Mica, $KH_2Al_3(SiO_4)_3$
- Kaolin, $H_2Al_2(SiO_4)_2,H_2O$

DISILICATE ($H_6Si_2O_7$)
- Serpentine, $Mg_3Si_2O_7,2H_2O$

METASILICATES (H_2SiO_3)
- Wollastonite, $CaSiO_3$
- Beryl, $Gl_3Al_2(SiO_3)_6$
- Talc (soapstone), $H_2Mg_3(SiO_3)_4$
- Asbestos, $Mg_3Ca(SiO_3)_4$

TRISILICATE ($H_4Si_3O_8$)
- Orthoclase (felspar), $KAlSi_3O_8$

It will be seen that the total valence of the metal units is equal to that of the acid radicals. Thus, in beryl there are six equivalents of glucinum (beryllium) and six of aluminium, taking the place of twelve units of hydrogen in $(H_2SiO_3)_6$.

Mica, which is obtained in large sheets from Farther India, is used in making lamp chimneys and as an insulator in electrical apparatus. **Kaolin,** or **clay,** like mica, is an acid orthosilicate. Garnets are pulverized in manganese steel crushers and used in making sandpaper.

Some of these minerals frequently occur mixed together as regular components of certain igneous rocks. Thus, **granite** (p. 2) is a more or less coarse mixture of quartz, mica, and felspar. Frequently the oblong, flesh-colored or white crystals of the last are very conspicuous. **Sandstone** is composed of sand cemented together by clay or by lime, and colored brown or yellow by ferric oxide.

The high melting-point of silica, compared with carbon dioxide, and the formation of these complex silicates, indicate that the oxide is highly associated $(SiO_2)_x$.

Boron B

As regards **chemical relations,** boron, being a uniformly trivalent element, is a member of the aluminium family (see Table of periodic system). Yet it is a pronounced non-metal, and its oxide and hydroxide are acidic: aluminium is a metal, and with its oxide and hydroxide basic properties predominate. Boron and its compounds really resemble carbon and silicon and their compounds in all chemical properties, excepting that of valence.

Occurrence. — Like silicon, boron is found in oxygen compounds, namely, in boric acid and its salts. Of the latter, sodium tetraborate $Na_2B_4O_7$, or borax, came first from India under the name of **tincal.** It constitutes a large deposit in Borax Lake in California. Colemanite, $Ca_2B_6O_{11},5H_2O$, from California, furnishes a large part of the commercial supply of compounds of boron.

Preparation. — When boric oxide is heated with powdered magnesium ($B_2O_3 + 3Mg \rightarrow 3MgO + 2B$), black, amorphous boron can be separated with some difficulty from the borides of magnesium in the resulting mixture. When excess of powdered aluminium is used, hard crystals of boron are formed.

Properties. — Boron unites with the same elements as does silicon (p. 425), but with somewhat greater activity. Like carbon (pp. 276, 355), it is also oxidized by hot, concentrated sulphuric or nitric acid, the product being boric acid. It interacts with fused potassium hydroxide, giving a borate:

$$2B + 6KOH \rightarrow 2K_3BO_3 + 3H_2.$$

Boron, when heated with nitrogen, unites to form the **nitride** BN, a white solid. When heated in the electric furnace with carbon, it forms a **carbide** B_6C. This substance is harder than carborundum, and stands next to the diamond in this respect (Appendix II).

The Halides of Boron. — By combined action of carbon and chlorine on boric oxide (p. 426), the **trichloride of boron** BCl_3 may be made. It is a liquid (b.-p. 18°) which fumes strongly in moist air, and is completely hydrolyzed by water.

Boron trifluoride BF_3 is made by the interaction of calcium fluoride and sulphuric acid with boron trioxide. The mode of preparation and the properties of the substance recall silicon tetrafluoride (p. 427). It interacts with water, like the latter, giving boric acid and **hydrofluoboric acid** HBF_4:

$$4BF_3 + 3H_2O \rightarrow B(OH)_3 + 3HBF_4.$$

Boric Acid and Boron Trioxide. — Boric acid (boracic acid), H_3BO_3 is somewhat volatile with steam, and is found in Tuscany in jets of water vapor (*soffioni*) which issue from the ground. Water, retained in basins of brickwork, is placed over the openings, and from this water, after evaporation, boric acid is obtained in crystalline form. As boric acid is a very feeble acid, and withal little soluble, it may also be made from sulphuric acid and concentrated borax solution. It crystallizes on cooling the mixture:

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \leftrightarrows Na_2SO_4 + 4H_3BO_3\downarrow.$$

Boric acid crystallizes from water in thin white plates, which are unctuous (like graphite and talc) to the touch. Its solubility in water is 4 parts in 100 at 19°, and 34 in 100 at 100°. The solution scarcely affects litmus. The green tint it confers on the Bunsen flame is used as a **test** for the acid. At 100° the acid slowly loses water, leaving **metaboric acid** HBO_2, and at 140° **tetraboric acid** is formed: $4HBO_2 - H_2O \rightarrow H_2B_4O_7$. Strong heating gives the **trioxide** B_2O_3, a glassy, white solid. When dissolved in water, all these dehydrated compounds revert to orthoboric acid H_3BO_3. The solution of boric acid in water is used as an antiseptic in medicine (half-saturated, 2 per cent solution), and sometimes as a preservative for milk and other foods.

Borates. — Borates derived from orthoboric acid are practically unknown. The most familiar salt is **borax** or **sodium tetraborate.** The decahydrate $Na_2B_4O_7,10H_2O$, which crystallizes from water at 27° in large, transparent prisms, and the pentahydrate which crystallizes at 56°, are both marketed. They are made by crystallization of native borax. In Germany, borax is prepared from boracite, found at Stassfurt, by decomposing a solution of the mineral with hydrochloric acid:

$$MgCl_2,2Mg_3B_8O_{15} + 12HCl + 18H_2O \rightarrow 7MgCl_2 + 16H_3BO_3.$$

The boric acid is dissolved in boiling water, and sodium carbonate is added: $4H_3BO_3 + Na_2CO_3 \rightarrow Na_2B_4O_7 + 6H_2O + CO_2$. In California it is made from colemanite by interaction with sodium carbonate.

Since boric acid is a feeble acid, borax is hydrolyzed by water, and the solution has a marked alkaline reaction (*cf.* p. 271). In a $0.1N$ solution (25°), 0.5 per cent is hydrolyzed.

When heated with oxides of metals, sodium tetraborate behaves like sodium metaphosphate (*cf.* p. 371), and is used in the form of **beads** in analysis. If its formula be written $2NaBO_2,B_2O_3$ (*cf.* p. 369) it will be seen that a considerable excess of the acid anhydride is contained in it, and that, therefore, a mixed metaborate may be formed by union with some basic oxide. Thus, with a trace of cupric oxide, the bead is tinged with blue, from the presence of a compound like $2NaBO_2,Cu(BO_2)_2$. In welding iron, borax is scattered on the parts, and combines with the oxide to form a fusible mixed borate, which is forced out by the pressure. Borax is also mixed with glass in making enamels for cooking utensils.

Exercises. — 1. Compare and contrast the elements carbon and silicon, and their corresponding compounds.

2. What would be the interaction between aqueous solutions of an ammonium salt and of sodium orthosilicate (*cf.* p. 429)? Why is ammonium silicate *completely* hydrolyzed by water?

CHAPTER XXXIII

THE BASE-FORMING ELEMENTS

In the present chapter a preliminary view of the chemistry of the metallic elements is given.

Physical Properties of the Metals.—Metals show what is commonly called a **metallic luster,** but, as a rule, they do so only when in compact form. Magnesium and aluminium exhibit it when powdered, but in this condition most metals are black.

The metals can all be obtained in **crystallized form,** when a fused mass is allowed to cool slowly and the unsolidified portion is poured off. In almost all cases the crystals belong to the regular system.

The metals vary in **specific gravity** from lithium, which is little more than half as heavy as water (sp. gr. 0.59), to osmium, whose specific gravity is 22.5. Those which have a specific gravity less than 5, namely, potassium, sodium, calcium, magnesium, aluminium, and barium, are called the **light metals,** and the others the **heavy metals.**

Most metals are **malleable,** and can be beaten into thin sheets without loss of continuity. Those which are allied to the non-metals, however, such as arsenic, antimony, and bismuth, are brittle. The order of the elements in respect to this property, beginning with the most malleable, is: Au, Ag, Cu, Sn, Pt, Pb, Zn, Fe, Ni.

The **tenacity** of the metals places them in an order different from the above. It is measured by the number of kilograms which a piece of the metal 1 sq. mm. in section can sustain without breaking. The values are as follows: Fe 62, Cu 42, Pt 34, Ag 29, Au 27, Al 20, Zn 5, Pb 2.

The **hardness** is measured by the ease with which the material may be scratched by a sharp, hard instrument. Potassium is as soft as wax, while chromium is hard enough to cut glass (Appendix II).

The **temperature** at which the metal **fuses** has an important bearing on its manufacture. Most of the following **melting-points** are only approximate:

Mercury	−39°	Zinc	419°	Cast iron	1150°
Potassium	62°	Antimony	630°	Manganese	1260°
Sodium	96°	Magnesium	651°	Nickel	1452°
Tin	232°	Aluminium	659°	Chromium	1520°
Bismuth	271°	Silver	960°	Iron (pure)	1530°
Cadmium	321°	Gold	1063°	Platinum	1755°
Lead	327°	Copper	1083°	Tungsten	3267°

It will be seen that mercury is a liquid, that potassium and sodium melt below the boiling-point of water, and that the metals down to the foot of the second column can be melted easily with the Bunsen flame.

The methods of manufacture and the treatment of metals are much influenced also by their **volatility.** The following are easily distilled: Mercury, b.-p. 357°; potassium and sodium, b.-p. about 700°; cadmium, b.-p. 770°; zinc, b.-p. 920°. Even the most involatile metals can be converted into vapor in the electric arc.

In many cases molten metals dissolve in one another, forming **alloys.** Some alloys are simply solid solutions. Sometimes, as in the case of lead and tin, mixtures can be formed in all proportions. Again, the solubility may be limited, as in the case of zinc and lead, where only 1.6 parts of the former dissolve in 100 parts of the latter. Frequently chemical compounds are formed. The colors of alloys are not the average of those of the constituents. Thus, the nickel alloy used in coining contains 75 per cent of copper and 25 per cent of nickel, yet it shows none of the color of the former.

Alloys in which mercury is one of the components are known as **amalgams** (Gk. *μάλαγμα*, a soft mass), and are formed with especial ease by the lighter metals. Of the common metals, iron is the least miscible with mercury.

The good **conductivity** of metals for **electricity** distinguishes them with some degree of sharpness from the non-metals. They show considerable variation amongst themselves, silver conducting sixty times as well as mercury. The following table gives the conductivities of the metals, expressed in terms of the number of meters of wire 1 sq. mm. in section which, at 15°, offer a resistance of one ohm:

Silver, cast	62.89	Nickel, cast	7.59
Copper, commercial	57.40	Iron, drawn	7.55
Gold, cast	46.30	Platinum	5.7–8.4
Aluminium, commercial	31.52	Steel	5.43
Zinc, rolled	16.95	Lead	4.56
Brass	14.17	Mercury	1.049

To compare these **conductivities** with those of solutions, it may be said that decinormal hydrochloric acid (p. 240) has a conductivity on the above scale of 0.035, or a thirtieth of that of mercury.

The **world's production (1913) of the metals** in metric tons of 1000 kilos. is approximately as follows:

Copper	1,000,000	Chromium	50,000	Gold	680
Zinc	1,000,000	Nickel	32,000	Bismuth	500
Lead	1,000,000	Silver	7,800	Cadmium	50
Tin	120,000	Tungsten	4,800	Platinum	9
Aluminium	79,000	Mercury	3,000		

General Chemical Relations of the Metallic Elements.—Since most of the compounds of the metals are ionogens, their solutions, except when the metal is a part of a compound ion, all contain the metal in the ionic state, and the resulting substances, such as potassium-ion and cupric-ion, have constant properties, irrespective of the nature of the negative ion with which they may be mixed. The properties of the ions, simple and compound, are much used in making tests in analytical chemistry. On the other hand, the chemical properties of the oxides and of the salts in the *dry state* are of importance in connection with metallurgy.

There are **three chemical properties** which are **characteristic of the metallic elements**. The first two of them have already been discussed somewhat fully.

1. The metals are able by themselves to form *positive* radicals of salts, and therefore to exist alone as positive ions (pp. 246, 296).

2. The oxides and hydroxides of the metals are basic (pp. 94, 296).

3. Each *typical* metal has at least one halogen compound which is little, if at all, hydrolyzed by water (p. 296). The same thing is true of nitrates and other salts involving active acids.

In reference to the third characteristic, the **non-hydrolysis of halides of typical metals,** a word of explanation is required. **Active bases** (hydroxides of typical metals), such as sodium hydroxide, give, with **feeble acids,** such as H_2S (p. 271), H_3PO_4 (p. 370), H_2CO_3 (p. 383), H_2SiO_3 (p. 428), and H_3BO_3 (p. 432), salts whose solutions are **alkaline in reaction.** This is due to hydrolysis. But **active bases** give, with **active acids,** such as HCl and HNO_3, salts whose solutions are **neutral in reaction.** This is the fact expressed in the third characteristic of the metallic elements. The **less active bases,** being hydroxides of less active metallic elements, give, with active acids, salts whose solutions are not neutral, but **acid in reaction.** Thus cupric chloride solution is feebly acid. This is because there is a tendency for the ions of the water to form the slightly dissociated molecules of the base:

$$Cu^{++} + 2OH^- + 2H^+ \rightarrow Cu(OH)_2 + 2H^+.$$

Finally, a salt derived from a **base and an acid, both** of which are **weak,** is also hydrolyzed. If the resulting base or acid is insoluble, the hydrolysis may go to completion. Aluminium carbonate and ammonium silicate (p. 429) are examples of salts which, for this reason, are completely hydrolyzed. The resulting mixture may have an acid or a basic reaction, if the acid or the base is sufficiently soluble and sufficiently active. Thus, ammonium sulphide $(NH_4)_2S$ solution is alkaline.

Aside from these points, many features in the behavior of metals and their compounds are summed up in the electromotive series (p. 260). Before proceeding farther, the reader should reread all the pages referred to above. He should also reëxamine the various kinds of chemical changes discussed on pp. 166, 197, 251 *et seq.* and particularly the varieties of ionic chemical change on p. 259.

Occurrence of the Metals in Nature. — The minerals from which metals are extracted are known as **ores.** They present a comparatively small number of different kinds of compounds. Most of the metals are found in more than one of these forms, so that in the following statement the same metal frequently occurs more than once.

When the metal occurs free in nature, it is said to be **native.**

Thus we have gold, silver, metals of the platinum group, copper, mercury, bismuth, antimony, and arsenic occurring native (*cf.* p. 60).

The metals whose **oxides** are important minerals are iron, manganese, tin, zinc, copper, and aluminium. The metals are obtained commercially from the oxides in each of these cases.

The metals whose **sulphides** are used as ores are iron, nickel, cobalt, antimony, lead, cadmium, zinc, copper, and mercury.

From the **carbonates** we obtain iron, lead, zinc, and copper. Several other metals, such as manganese, magnesium, barium, strontium, and calcium occur in larger or smaller quantities in the same form of combination.

The metals which occur as **sulphates** are those whose sulphates are not freely soluble, namely, lead, barium, strontium, and calcium.

Compounds of metals with the **halogens** are not so numerous. Silver chloride furnishes a limited amount of silver. Sodium and potassium chlorides are found in the salt-beds.

The natural *silicates* are very numerous, but few are used for the preparation of the metals. Many are employed for other commercial purposes, kaolin (p. 430) being a conspicuous example.

Methods of Extraction from the Ores. — The art of extracting metals from their ores is called **metallurgy**. Where the metal is **native,** the process is simple, since melting away from the matrix (p. 264) is all that is required. Frequently a **flux** is added. A flux usually is a substance which interacts with infusible materials to give fusible ones. It combines with the matrix, giving a fusible **slag** (resembling glass). Since the slag is a melted salt, usually a silicate, and does not mix at all with the molten metal, separation of the products is easily effected. When the ore is a *compound,* the metal has to be liberated by our furnishing a material capable of combining with the other constituent. The details of the process depend on various circumstances. Thus the volatile metals, like zinc and mercury, are driven off in the form of vapor, and secured by condensation. The involatile metals, like copper and iron, run to the bottom of the furnace and are tapped off.

Where the ore is an **oxide** it is usually reduced by heating with carbon in some form. This holds for the oxides of iron and copper. Some oxides are not reducible by carbon in an ordinary furnace. Such are the oxides of calcium, strontium, barium, magnesium, aluminium, and the members of the chromium group. At the temperature of the electric furnace even these may be reduced, but the carbides are formed under such circumstances, and the metals are more easily obtained otherwise. Recently, heating the pulverized oxide with finely powdered aluminium has come into use, particularly for operations on a small scale. Iron oxide is easily reduced by this means, and even the metals manganese and chromium may be liberated from their oxides quite readily by this action. On account of the great amounts of heat liberated, this procedure has received the name **aluminothermy** (*q.v.*).

When the ore is a **carbonate,** it is first heated strongly to drive out the carbon dioxide (*cf.* p. 381): $FeCO_3 \rightleftarrows FeO + CO_2\uparrow$, and then the oxide is treated according to one of the above mentioned methods. When the ore is a **sulphide,** it has to be calcined (p. 275), in order to remove the sulphur, and the resulting oxide is then reduced.

Chlorides and **fluorides** of the metals can be decomposed by heating with metallic sodium. This method was formerly employed in the making of magnesium and aluminium.

The metals which are not readily secured in any of the above ways can be obtained easily by **electrolysis** of the fused chloride or of some other compound. Aluminium is now manufactured entirely by the electrolysis of a solution of aluminium oxide in molten cryolite.

Compounds of the Metals: Oxides and Hydroxides.— The **oxides** may be made by direct burning of the metal, by heating the nitrates (*cf.* p. 351), the carbonates (*cf.* p. 381), or the hydroxides: $Ca(OH)_2 \rightleftarrows CaO + H_2O\uparrow$. They are practically insoluble in water, although the oxides of the metals of the alkalies and of the metals of the alkaline earths interact with water rapidly to give the hydroxides. Oxides are usually stable. Those of gold, platinum, mercury, and silver decompose when heated, yet with increasing difficulty in this order. The metals, like the non-metals, frequently give several different oxides. Those of the univalent metals (having the form K_2O), if we leave cuprous oxide and aurous oxide out of account, have the most strongly basic qualities. Those of the bivalent metals of the form MgO, when this is the only oxide which they furnish, are base-forming. Those of the trivalent metals of the form Al_2O_3, known as **sesquioxides** (Lat. *sesqui-*, one-half more), are the least basic of the basic oxides. The oxides of the forms SnO_2, Sb_2O_5, CrO_3, and Mn_2O_7, in which the metals have valences from 4 to 7, are mainly acid-forming oxides, although the same elements usually have other lower oxides, which are basic.

The **hydroxides** are formed, in the cases of the metals of the alkalies and alkaline earths, by direct union of water with the oxides. They are produced also by double decomposition when a soluble hydroxide acts upon a salt (*cf.* p. 252). All hydroxides, except those of the alkali metals, lose the elements of water when heated, and the oxide remains. In some cases the loss takes place by stages, just as was the case with orthophosphoric acid (p. 368). Thus lead hydroxide $Pb(OH)_2$ (*q.v.*) first gives the hydroxide $Pb_2O(OH)_2$, then $Pb_3O_2(OH)_2$, and then the oxide PbO. The hydroxides of mercury and silver, if they are formed at all, are evidently unstable, for, when either material is dried, it is found to contain nothing but the corresponding oxide. The hydroxides, with the exception of those of the metals of the alkalies and alkaline earths, are all little soluble in water.

Compounds of the Metals: Salts. — It may be said, in general, that each metal may form a salt by combination with each one of the acid radicals. In the succeeding chapters we shall describe only those salts which are manufactured commercially, or are of special interest for some other reason. The various salts will be described under each metal. Here, however, a few remarks may be made about the characteristics of the more common groups of salts.

The **chlorides** may be made by the direct union of chlorine with the metal (*cf.* p. 160), or by the combined action of carbon and chlorine upon the oxide (*cf.* p. 426). The latter method is used in making chromium chloride. The general methods for making any salt (p. 146), such as the interaction of a metal with an acid, or of the oxide, hydroxide, or another salt with an acid, or the double decomposition of two salts, may be used also for making chlorides. The chlorides are for the most part soluble in water.

Silver chloride, mercurous chloride, and cuprous chloride are almost insoluble, however, and lead chloride is not very soluble. Most of the chlorides of metals dissolve without decomposition, but hydrolysis is conspicuous in the case of the chlorides of the trivalent metals, such as aluminium chloride and ferric chloride (*cf.* p. 437). The chlorides of some of the bivalent metals are hydrolyzed also, but, as a rule, only when they are heated with water. This is the case with the chlorides of magnesium, calcium, and zinc. Most of the chlorides are stable when heated, but those of the noble metals, particularly gold and platinum, are decomposed, and chlorine escapes. The chlorides are usually the most volatile of the salts of a given metal, and so are preferred for the production of the spectrum of the metal. Some metals, for example iron, form two or more different chlorides. Indium gives $InCl$, $InCl_2$, and $InCl_3$.

The **sulphides** are formed by the direct union of the metal with sulphur, or by the action of hydrogen sulphide or of some soluble sulphide upon a solution of a salt (*cf.* p. 273). In one or two cases they are made by the reduction of the sulphate with carbon. The sulphides, except those of the alkali metals, are but little soluble in water. The sulphides of aluminium and chromium are hydrolyzed completely by water, giving the hydroxides, and those of the metals of the alkaline earths are partially hydrolyzed (*cf.* p. 273).

The **carbides** are usually formed in the electric furnace by interaction of an oxide with carbon (*cf.* p. 379). Some of them are decomposed by contact with water, after the manner of calcium carbide, giving a hydroxide and a hydrocarbon. Of this class are lithium carbide Li_2C_2, barium and strontium carbides BaC_2 and SrC_2, aluminium carbide Al_4C_3, manganese carbide MnC, and the carbides of potassium and glucinum. Others, such as those of molybdenum Mo_2C and chromium Cr_3C_2, are not affected by water.

The **nitrates** may be made by any of the methods used for preparing salts. They are *all* at least fairly soluble in water.

The **sulphates** are made by the methods used for making salts, and in some cases by the oxidation of sulphides. They are all soluble in water, with the exception of those of lead, barium, and strontium. Calcium sulphate is meagerly soluble.

The **carbonates** are prepared by the methods used for making salts. They are all insoluble in water, with the exception of those of sodium and potassium. The hydroxides of aluminium and tin are so feebly basic that they do not form stable carbonates (*cf.* pp. 429, 437).

The **phosphates** and **silicates** are prepared by the methods used in making salts. The former are obtained also by special processes already described (p. 371). With the exception of the salts of sodium and potassium, all the salts of both these classes are insoluble.

For the **exact solubilities** of a large number of **bases and salts** at 18°, see the **Table inside the cover,** at the front of this book. **Solubilities at all temperatures** are shown in the **diagram,** Fig. 58, p. 131.

Exercises. — 1. What do we mean by saying that an oxide is strongly or feebly basic, or that it is acidic?

2. What is meant by the same terms when applied to an hydroxide?

3. Compare the molar solubilities at 18°, (*a*) of the halides of silver, and (*b*) of the carbonates and (*c*) oxalates of the metals of the alkaline earths, noting the relation between solubility and atomic weight.

4. What is the molar concentration of chloride-ion in saturated solutions of silver chloride and lead chloride at 18°, assuming complete ionization in these very dilute solutions?

CHAPTER XXXIV

THE METALLIC ELEMENTS OF THE ALKALIES: POTASSIUM AND AMMONIUM

The metals of this family, with their atomic weights, are:

Lithium, Li	6.9	Rubidium, Rb	85.5
Sodium, Na (Ger. *natrium*)	23.0	Cæsium, Cs	132.8
Potassium, K (Ger. *kalium*)	39.1		

The Chemical Relations of the Metallic Elements of the Alkalies. — The metals which are chemically most active are included in this group, and the activity increases with rising atomic weight, cæsium being the most active positive element of all. A freshly cut surface of any of these metals tarnishes by oxidation as soon as it is exposed to the air. All of these metals decompose water violently (*cf.* p. 60), liberating hydrogen. The hydroxides which are formed by this action are exceedingly active bases, that is to say, they give a relatively large concentration of hydroxide-ion in solutions of a given molecular concentration (p. 243). In the dry form these hydroxides are not decomposed by heating, while the hydroxides of all other metals lose water more or less easily. In all their compounds the metals of the alkalies are univalent.

The compounds of ammonium are discussed in connection with those of potassium, to which they present the greatest resemblance.

The solubilities are often decisive factors in connection with the preparation and use of salts. The reader will find most of these in the table on the inside of the cover, at the front of this book, or in the diagram on p. 131, and, as a rule, the values will not be repeated in the descriptive paragraphs.

Potassium K

Occurrence. — Silicates containing potassium, such as felspar and mica (p. 430), are constant constituents of volcanic rocks. These minerals are not used commercially as sources of potassium compounds. The salt deposits (see below) contain potassium chloride, alone (sylvite) and in combination with other salts, and most of the compounds of potassium are manufactured from this material. Part of our potassium nitrate, however, is purified Bengal saltpeter (p. 347). Potassium sulphate occurs also in the salt layers.

Preparation. — Potassium was first made by Davy (1807) by bringing the wires from a battery in contact with a piece of moist potassium hydroxide. Globules of the metal appeared at the negative wire. Electrolytic processes have now come back into use, commercially, molten potassium chloride being the substance decomposed. Castner's reduction process involves the heating of potassium hydroxide with a spongy mass of carbide of iron (CFe_2). The potassium passes off as vapor, and is condensed:

$$6KOH + 2C \rightarrow 2K_2CO_3 + 3H_2 + 2K.$$

Physical and Chemical Properties. — Potassium is a silver-white metal (m.-p. 62°). It boils at 720°, giving a green vapor.

The density of the vapor shows the molecular weight of potassium to be about 40, so that the vapor is a monatomic gas. The element unites violently with the halogens, sulphur, and oxygen. In consequence of the latter fact it is usually kept under petroleum, an oil which neither contains oxygen itself, nor dissolves a sufficient amount of moisture from the air to permit much oxidation of the potassium to take place. A white, crystalline **hydride** KH is formed when hydrogen is passed over potassium heated to 360°. When thrown into water it gives potassium hydroxide, and the hydrogen is liberated.

Potassium Chloride KCl. — Sea-water and the waters of salt lakes contain a relatively small proportion of potassium compounds. During the evaporation of such waters, however, the potassium compounds tend to accumulate in the mother-liquor while sodium chloride is being deposited on the bottom. Hence the upper layers of salt deposits are the richest in compounds of potassium. Thus, at Stassfurt, near Magdeburg, there is a thickness of more than a thousand meters of common salt. Above this are 25–30 meters of salt layers in which the potassium salts are chiefly found.

The chief forms in which potassium chloride is found in the salt beds are sylvite KCl and carnallite $KCl,MgCl_2,6H_2O$. The latter salt is heated with a small amount of water, or with a mother-liquor obtained from a previous operation and containing sodium and magnesium chlorides. From the clear liquid, when it cools, potassium chloride is deposited first and then carnallite. The former is taken out and purified, and the latter goes through the process again. This potassium chloride is the source from which our other potassium compounds are made. It is also our chief potassium-bearing fertilizer. It is a white substance crystallizing in cubes, melting at about 750°, and slightly volatile at high temperatures.

Recently, the giant kelps of the Pacific coast have been used as a source of potassium chloride. The dried seaweed contains 9 per cent of this salt and about 0.1 per cent of iodine.

The Other Halides of Potassium. — When iodine is heated in a strong solution of potassium hydroxide, potassium iodate and **potassium iodide** are both formed (p. 318):

$$6KOH + 3I_2 \rightarrow 5KI + KIO_3 + 3H_2O.$$

The dry residue from evaporation is heated with powdered carbon to reduce the iodate, and all the iodide can then be purified by recrystallization. The salt forms large, somewhat opaque cubes (m.-p. 623°). It is used in medicine and for precipitating silver iodide AgI in photography (*q.v.*).

The aqueous solution takes up free iodine, forming KI_3, in equilibrium with dissolved iodine: $I_3^- \rightleftarrows I^- + I_2$ (dslvd). It is used in testing for starch, and in reactions in which a solution of free iodine is required.

Potassium bromide KBr may be made in the same way as the iodide. It crystallizes in cubes. It is used in medicine and for precipitating silver bromide in making photographic plates (*q.v.*).

The **fluoride of potassium** K_2F_2 may be obtained by treating the carbonate or hydroxide with hydrofluoric acid. It is a deliquescent, white salt. When treated with an equimolecular quantity of hydrofluoric acid it forms **potassium-hydrogen fluoride** KHF_2, a white salt which is also very soluble.

Potassium Hydroxide KOH. — This compound, known also as **caustic potash,** and colloquially as potassium hydrate, was formerly made entirely by boiling potassium carbonate with calcium hydroxide suspended in water (milk of lime):

$$\left.\begin{array}{r} \mathrm{Ca(OH)_2(solid) \rightleftarrows Ca(OH)_2(dslvd) \rightleftarrows 2OH^- + Ca^{++}} \\ \mathrm{K_2CO_3 \rightleftarrows 2K^+ + CO_3^=} \end{array}\right\} \rightleftarrows \mathrm{CaCO_3(dslvd) \rightleftarrows CaCO_3\ (solid).}$$

The operation is conducted in iron vessels, because porcelain, being composed of silicates, interacts with solutions of bases. On account of the very limited solubility of the calcium hydroxide (0.17 g. in 100 g. Aq), the water takes up fresh portions into solution only when the part dissolved has already undergone chemical change. The calcium carbonate which is precipitated is, however, still more insoluble (0.0013 g. in 100 g. Aq), and hence the action goes forward. After the precipitate has settled, the potassium hydroxide is obtained by evaporation of the clear liquid, $K^+ + OH^- \rightarrow KOH$.

Potassium hydroxide is now manufactured by electrolytic processes. When a solution of potassium chloride is electrolyzed, chlorine is liberated at the anode, and hydrogen and potassium hydroxide at the cathode (p. 228). These two sets of products must be kept apart, since by their interaction potassium hypochlorite and potassium chloride would be formed (*cf.* p. 308). In the Castner-Kellner apparatus (Fig. 112), which serves for making either potassium or sodium hydroxide, the two end compartments are filled with potassium chloride solution (or brine) and contain the graphite anodes. The central compartment contains potassium hydroxide solution and the iron cathode. The positive

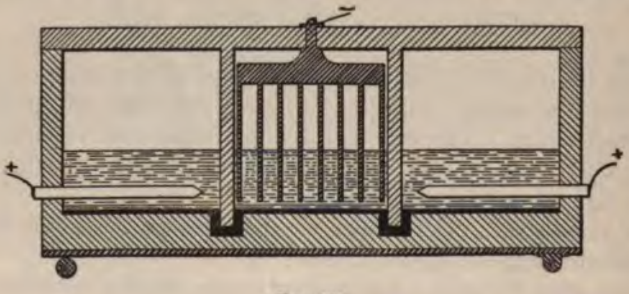


Fig. 112.

current enters by the anodes, and the chlorine is therefore attracted to and liberated upon the graphite: $2Cl^- + 2\oplus \rightarrow Cl_2$. After rising through the liquid, it is collected for the manufacture of liquefied chlorine or of bleaching powder. The ions of potassium (or of sodium) are discharged upon a layer of mercury which covers the whole floor of the box, and the free metal dissolves in the mercury, forming an amalgam (p. 435). The layer of mercury extends beneath the partitions, and a slight rocking motion given to the cell causes the amalgam to flow below the partition into the central compartment. Here the potassium leaves the mercury in the form of potassium-ion and is attracted by the cathode. Upon this, hydrogen from the water is discharged, and the residual hydroxide-ion, together with the metal-ion, constitute potassium or sodium hydroxide:

$$2K^+ + 2H^+ + 2OH^- + 2\ominus \rightarrow 2K^+ + 2OH^- + H_2.$$

A slow influx of salt solution to the end compartments, and overflow of the alkaline solution in the central cell, are maintained. The overflowing liquid contains 20 per cent of the alkali. Since there is no undecomposed chloride present in the part of the solution which contains the hydroxide, simple evaporation to dryness furnishes the solid alkali. Other forms of electrolytic cells, such as the Briggs, and the Townsend-Baekeland cells, are also largely in use.

Potassium hydroxide is exceedingly soluble in water, and consequently, instead of being crystallized from solution, the molten residue from evaporation is cast in sticks. The hydroxide is highly deliquescent. It also absorbs carbon dioxide from the air, giving potassium carbonate. Solutions of the hydroxide have an exceedingly corrosive action upon the flesh, resolving it into a slimy mass by decomposing the proteins. In solution, the base is highly ionized, furnishing a high concentration of hydroxide-ion. Commercially, it is chiefly employed in the making of soft soap.

Potassium oxide K_2O may be made by heating potassium nitrate with potassium in a vessel from which air is excluded: $2KNO_3 + 10K \rightarrow 6K_2O + N_2$. It interacts violently with water, giving the hydroxide. When exposed to the air it unites spontaneously with oxygen, and a yellow **peroxide** K_2O_4 is formed. The same peroxide is formed when potassium burns in air or oxygen.

Potassium Chlorate $KClO_3$.—The preparation of this salt by interaction of potassium chloride with calcium chlorate has already been described (p. 313). It is also made by electrolysis of potassium chloride solution, the potassium hydroxide and chlorine which are liberated being precisely the materials required. All that is necessary is to use a warm, concentrated solution and to provide for the mixing of the materials generated at the electrodes. The salt crystallizes out when the solution cools.

Potassium chlorate crystallizes in monoclinic plates. It melts at about 334°, and at a temperature slightly above this the visible liberation of oxygen begins (*cf.* pp. 27, 29). On account of the ease with which its oxygen is liberated, the salt is employed in making fireworks and as a component of the heads of Swedish matches. It is also used in medicine.

Potassium perchlorate $KClO_4$, formed by the heating of the chlorate (p. 315), gives white crystals belonging to the rhombic system.

By adding chlorine-water to potassium carbonate solution, a mixture of the chloride and **potassium hypochlorite** is formed:

$$HCl + HClO + K_2CO_3 \rightarrow KCl + KClO + H_2O + CO_2.$$

The carbonic acid, however, is not completely displaced by the HClO, which is a feeble acid. Hence, the solution is used, under the name *eau de Javel* (often misspelt Javelle), in the household for removing stains.

The mode of preparing **potassium bromate** $KBrO_3$ and **potassium iodate** KIO_3 has already been described (p. 318). Potassium iodate may be made also very conveniently by melting together potassium chlorate and potassium iodide at a low temperature. The iodate is much less soluble (see Table) than the chloride, and the mixture may be separated by crystallization from water.

Potassium Nitrate KNO_3.—The formation of this salt in nature and its mode of extraction and purification have already been described (p. 347). This source of supply proved insufficient, for the first time, during the Crimean war (1852–55), and a method of manufacture from Chile saltpeter (sodium nitrate), which is a much cheaper substance, was introduced. Sodium nitrate and potassium chloride are *heated* with *very little* water, and the sodium loride produced by the action, which is a reversible one, is by far the least soluble of the four salts (see Diagram, p. 131). On the other hand, in the hot water, the potassium nitrate is by far the most soluble. Hence the hot liquid, quickly drained from the crystals through canvas, contains the required salt, and most of the sodium chloride is in the form of a precipitate. If the solubility curve of potassium nitrate (p. 131) is examined, it will be seen that this salt is but slightly soluble in cold water, and hence most of it is deposited when the solution cools. The crystals are mixed with little sodium chloride, for, as the curve shows, common salt is little less soluble at 10° than it is at 100°.

Potassium nitrate gives long prisms belonging to the rhombic system (Fig. 113). It melts at about 340°, and when more strongly heated gives off oxygen, leaving potassium nitrite (p. 356). Although it does not form a hydrate, the crystals enclose small portions of the mother-liquor, and consequently contain both water and impurities. When heated, the crystals fly to pieces explosively (**decrepitate**), on account of the vaporization of this water. Many substances which form large crystals and do not melt at a low temperature, behave in the same way and for the same reason. In consequence of this, the purest salt is made by violent stirring of the solution during the operation of crystallization, the result being the formation of a crystal-meal.

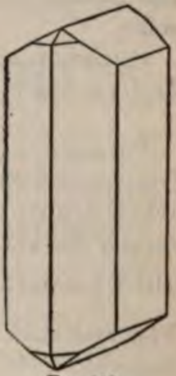


Fig. 113.

Potassium nitrate is used chiefly in the manufacture of **gunpowder,** which contains 75 per cent of the highly purified salt. The other components are 10 per cent of sulphur, 14 per cent of charcoal, and about 1 per cent of water. The ingredients are intimately mixed in the form of paste, and the material when dry is broken up and sifted, grains of different sizes being used for different purposes. The chemical action which takes place when gunpowder is fired in an open space gives chiefly potassium sulphide, carbon dioxide, and nitrogen:

$$2KNO_3 + 3C + S \rightarrow K_2S + 3CO_2 + N_2.$$

The explosion occurring in firearms follows a much more complex course. and half of the solid product is said to be potassium carbonate (a solid, hence the smoke). One gram yields 264 c.c. of gases (0° and 760 mm.), and a much larger volume at the temperature of the explosion, and gives 660 calories. The pressure, at the temperature of the explosion, if the gases could be confined within the volume originally occupied by the gunpowder, would reach about forty-four tons per square inch. In recent years, except in mining, common gunpowder has been displaced largely by **smokeless powder** (pp. 358, 359), which, in decomposing, produces no solids.

Potassium nitrate is used also in preserving ham and corned beef, on which it confers a red color.

Potassium Carbonate K_2CO_3.—This salt is manufactured from potassium chloride, from the Stassfurt deposits. The chloride is heated with magnesium carbonate (magnesite), water, and carbon dioxide *under pressure:*

$$2KCl + 3MgCO_3 + CO_2 + 5H_2O \rightarrow 2KHMg(CO_3)_2,4H_2O + MgCl_2.$$

The hydrated mixed salt separates from the liquid containing magnesium chloride and is decomposed by heating with water at 120°. The product is a solution of potassium carbonate, from which the precipitated magnesium carbonate is removed by filtration and used over again. In some districts potassium carbonate is still extracted from wood-ashes, its original source and the origin of its name, **potash.** The sugar beet takes up a considerable amount of potash from the soil, and the extract, after removal of the sugar, is evaporated and calcined. Wool scourings, when evaporated and calcined, also afford a small supply.

This salt is usually sold in the form of an anhydrous powder (m.-p. over 1000°). When crystallized from water it gives a hydrate $2K_2CO_3,3H_2O$. It is deliquescent. Its aqueous solution, like that of sodium carbonate (*cf.* p. 383), has a marked alkaline reaction. The commercial name of the substance is **pearl ash.** It is used in making soft soap and hard (*i.e.*, difficultly fusible) glass. It is also employed, by interaction with acids, in making salts of potassium.

The use of the **bicarbonate** $KHCO_3$ in purifying carbon dioxide has already been mentioned (p. 381). Before the nineteenth century, this salt was used under the name **saleratus** (Lat. *aerated* *salt*), a name now sometimes given the baking soda $NaHCO_3$ which has displaced it.

Potassium Cyanide KNC. — This salt is made by heating dry potassium ferrocyanide (*q.v.*):

$$K_4Fe(CN)_6 \rightarrow 4KNC + Fe + 2C + N_2.$$

When the residue is extracted with water, only the potassium cyanide dissolves, and it is easily crystallized in pure form from the solution.

Potassium cyanide is extremely soluble in water, and is therefore deliquescent. Its poisonous qualities are equal to those of hydrocyanic acid. The acid is so feeble as to be liberated both by the moisture and by the carbon dioxide of the air, and hence this salt always has an odor of hydrocyanic acid. Potassium cyanide was used in electroplating (*q.v.*), and in extracting gold (*q.v.*) from its ores, but has been displaced by sodium cyanide NaNC, which is now less expensive.

The preparation of **potassium cyanate** KCNO, a white, easily soluble salt, and of **potassium thiocyanate** KCNS, a white, deliquescent salt, have already been described (p. 421).

The Sulphate and Bisulphate. — Potassium sulphate K_2SO_4 is a constituent of several double salts found in the Stassfurt deposits. It is extracted from **schoenite** $MgSO_4,K_2SO_4,6H_2O$ and **kainite** $MgSO_4,MgCl_2,K_2SO_4,6H_2O$. The former is treated with potassium chloride and comparatively little water, whereupon the relatively insoluble potassium sulphate crystallizes out, and the magnesium chloride remains in the mother-liquor. The crystals belong to the rhombic system, contain no water of crystallization, and melt at 1066°. This salt is employed in preparing alum (*q.v.*) and is much used as a **fertilizer**. Since plants take up solutions through their cell walls, they can absorb soluble compounds only. They are, therefore, dependent, for the potassium compounds which they require, upon the weathering out of soluble potassium compounds from insoluble silicates containing potassium (p. 430) found in the soil. The weathering takes place too slowly to furnish a sufficient supply for many crops, particularly that of the sugar-beet. Hence potassium sulphate is mixed directly with the soil.

Potassium-hydrogen sulphate (bisulphate) $KHSO_4$ is made by the action of sulphuric acid upon potassium sulphate: $K_2SO_4 + H_2SO_4 \rightarrow 2KHSO_4$. It crystallizes from water, in which it is very soluble, in tabular crystals. Its properties are similar to those of sodium bisulphate, which have already been described (p. 288).

Sulphides of Potassium. — By the treatment of a solution of potassium hydroxide with *excess* of hydrogen sulphide, a solution of **potassium-hydrogen sulphide** is obtained. Evaporation of the solution gives a deliquescent, solid hydrate $2KHS,H_2O$. When the solution, before evaporation, is treated with an equivalent amount of potassium hydroxide, and the water is driven off, **potassium sulphide** K_2S remains behind (*cf.* p. 270):

$$KHS + KOH \rightleftarrows K_2S + H_2O.$$

Considerable amounts of sulphur can be dissolved in solutions of either of these sulphides. By evaporation of the resulting yellow liquids, various **polysulphides** have been obtained. These are probably K_2S_5, or mixtures of the pentasulphide with K_2S (*cf.* p. 274). Similar substances are produced, as a result of the liberation and recombination of sulphur, when the solutions are exposed to the oxidizing action of the air:

$$2KHS + O_2 \rightarrow 2KOH + 2S.$$

Properties of Potassium-ion K^+: Analytical Reactions. — The positive ionic material of the potassium salts is a colorless substance. It unites with all negative ions, and most of the resulting compounds are fairly soluble. For its **recognition** we add solutions containing those ions which give with it the least soluble salts. Thus, with chloroplatinic acid H_2PtCl_6 it gives a yellow precipitate of potassium chloroplatinate K_2PtCl_6. Since nearly one part of this salt dissolves in 100 parts of water, the test is far from being a delicate one. Picric acid (p. 349) gives potassium picrate $KC_6H_2(NO_2)_3O$, which is much less soluble in water (0.4 parts in 100 at 15°). Perchloric acid and hydrofluosilicic acid likewise give somewhat insoluble salts of potassium. **Potassium-hydrogen tartrate** $KHC_4H_4O_6$ is precipitated by the addition of tartaric acid to a sufficiently concentrated solution of a potassium salt. The neutral tartrate $K_2C_4H_4O_6$ is much more soluble. The latter may be obtained by treating the precipitate with a solution of potassium hydroxide. Addition of an acid to this solution causes reprecipitation of the bitartrate.

A much more delicate test for the recognition of a potassium compound consists in the examination by means of the **spectroscope** of the light given out by a Bunsen flame, in which a little of the salt is held upon a platinum wire. When the amount of potassium is considerable, and no other substance which would likewise color the flame is present to mask the effect, the violet tint is recognizable by the eye.

Rubidium and Cæsium. — In 1860 Bunsen discovered several new lines in the spectrum given by materials derived from the salts in Dürkheim mineral water. Two new elements of the alkali group were found to cause their presence, and were named, from the colors of the lines which they gave, rubidium (red) and cæsium (blue). Rubidium is obtainable with relative ease from the mother-liquors of the Stassfurt works.

The metals may be obtained by heating their hydroxides with magnesium powder. The hydroxides of these two elements are more active as bases than is potassium hydroxide. Their salts are very much like those of potassium.

AMMONIUM

The compounds of ammonium claim a place with those of the alkali metals because in aqueous solution they give ammonium-ion NH_4^+, a substance which in its behavior closely resembles potassium-ion. Some of the special properties peculiar to ammonium compounds, and particularly the properties of ammonium hydroxide NH_4OH, have been discussed in detail already (pp. 343–345).

Salts of Ammonium. — **Ammonium chloride** NH_4Cl, known commercially as **salammoniac,** like all the other compounds of ammonium, is prepared from the ammonia dissolved by the water used to wash illuminating gas (p. 411), or that obtained from by-product coke ovens (p. 411). It is purified by sublimation, and then forms a compact fibrous mass. At 337.8° its vapor exercises one atmosphere pressure, and is dissociated into ammonia and hydrogen chloride to the extent of 62 per cent (p. 345).

Ammonium nitrate NH_4NO_3 is a white crystalline salt which may be made by the interaction of ammonium hydroxide and nitric acid. When heated gently (m.-p. 166°) it decomposes, giving nitrous oxide and water (p. 357). It is used as an ingredient in fireworks and explosives.

When ammonium hydroxide is treated with excess of carbon dioxide the solution gives, on evaporation, **ammonium bicarbonate** NH_4HCO_3. This is a white crystalline salt which is fairly stable at the ordinary temperature. It has, however, a faint odor of ammonia, and its dissociation becomes very rapid when slight heat is applied. When a solution of this salt is treated with ammonium hydroxide, the **normal carbonate** $(NH_4)_2CO_3$ is formed. But this salt, when left in an open vessel, loses ammonia very rapidly, and leaves the bicarbonate behind.

Ammonium thiocyanate NH_4NCS (*cf.* p. 421) is a white salt which finds some application in analysis.

Ammonium sulphate $(NH_4)_2SO_4$ is a white salt which is used chiefly as a fertilizer. By electrolysis of a concentrated solution of the **bisulphate** NH_4HSO_4, ammonium **persulphate** $(NH_4)_2S_2O_8$, which is less soluble, is formed and crystallizes out (*cf.* p. 291).

Solutions of **ammonium-hydrogen sulphide** NH_4HS and **ammonium sulphide,** $(NH_4)_2S$, made by passing hydrogen sulphide gas into ammonium hydroxide, are much used in analysis. The sulphide is almost completely hydrolyzed by water into the acid sulphide and ammonium hydroxide, its behavior being like that of sodium sulphide (p. 271):

$$\left.\begin{array}{r} 2NH_3 + H_2S \rightleftarrows (NH_4)_2S \leftrightarrows 2NH_4^+ + S^= \\ H_2O \leftrightarrows OH^- + H^+ \end{array}\right\} \leftrightarrows HS^-.$$

It is used for the precipitation of sulphides, such as zinc sulphide ZnS, which are insoluble in water. Although the $S^=$ ions are not numerous at any moment, disturbance of the equilibrium by their removal, when they pass into combination, causes displacements which result in the generation of a continuous supply. The liquid smells strongly of ammonia and hydrogen sulphide, on account of the dissociation of the parent molecules by reversal of the above equilibria.

The solutions, when pure, are colorless. They dissolve free sulphur, giving yellow **polysulphides** similar to those of potassium (p. 452). The same yellow substances are also obtained by gradual oxidation of ammonium sulphide, when the solution of this salt is allowed to stand in a bottle from which the air is imperfectly excluded.

Ammonium Amalgam. — When a salt of ammonium is decomposed by electrolysis the NH_4^+, upon its discharge, ordinarily gives ammonia and hydrogen, and no substance NH_4 is obtained. If, however, a pool of mercury is used as the negative electrode, the NH_4 forms an amalgam with it, and there seems to be no doubt that this substance is actually present in solution in the mercury. While the amalgam is being formed it swells up and gives off the decomposition products above mentioned, so that the existence of the substance is only temporary. The same material may be obtained by putting sodium amalgam into a strong solution of a salt of ammonium. The action is a displacement of one ion by another (p. 259):

$$\text{Na(dslvd in mercury)} + NH_4^+ \rightarrow NH_4\text{(dslvd in mercury)} + Na^+.$$

This behavior is interesting since it is in harmony with the idea that ammonium, if it could be isolated, would have the properties of a metal. Substances other than metals are not miscible with mercury.

Ammonium-ion NH_4^+: Analytical Reactions. — Ionic ammonium is a colorless substance. It unites with negative ions, giving salts, which, in the majority of cases, are soluble. Ammonium chloroplatinate $(NH_4)_2PtCl_6$, and to a less extent ammonium-hydrogen tartrate $NH_4HC_4H_4O_6$, are insoluble compounds, and their precipitation is used as a test. The surest means of recognizing ammonium compounds, however, consists in adding a soluble base to the substance (*cf.* p. 345). The ammonium hydroxide, which is thus formed, gives off ammonia, and the latter may be detected by its odor.

Exercises. — 1. What kind of metals will, in general, interact with solutions of bases (*cf.* p. 296)?

2. Why should a mixture of potassium chlorate and antimony trisulphide be explosive?

3. How should you set about making, (*a*) a borate of potassium, (*b*) potassium pyrophosphate, (*c*) ammonium nitrite, (*d*) ammonium chlorate, (*e*) ammonium iodide?

CHAPTER XXXV

SODIUM AND LITHIUM. IONIC EQUILIBRIUM CONSIDERED QUANTITATIVELY

SODIUM chloride forms more than two-thirds of the solid matter dissolved in sea-water, and the great salt deposits are largely composed of it. Sea-plants contain mainly sodium salts of organic acids, just as land-plants contain potassium salts. Chile saltpeter and albite (a soda feldspar) are important minerals.

Compounds of sodium are usually cheaper than the corresponding ones of potassium. Also, since the atomic weight of sodium is 23, against 39 for potassium, a smaller weight of the sodium compound will produce the same chemical result. For these two reasons, sodium compounds, except in special cases, are always used for commercial purposes.

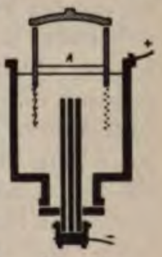


Fig. 114.

Preparation. — Sodium was first made by Davy (1807) by electrolysis of moist sodium hydroxide. It is manufactured by the electrolysis of fused sodium hydroxide by a method invented by Castner. The negative electrode projects through the bottom of the iron vessel containing the fused hydroxide (Fig. 114), and here the sodium and hydrogen are liberated. This electrode is surrounded by a wire-gauze partition to permit circulation of the fused mass, but prevent escape of the globules of sodium. This is surmounted by a bell-shaped vessel of iron. The positive electrode is an iron cylinder surrounding the gauze. The sodium and hydrogen liberated at the cathode, being lighter than the fused mass, ascend into the iron vessel (at *A*), under the edge of which the hydrogen escapes. Oxygen is set free at the anode. The top is closed, to prevent the sodium from burning. The melted sodium is ladled into molds, like candle molds.

Properties.—Sodium is a soft, shining metal, melting at 96° and boiling at 742°. The green vapor is a monatomic gas. The general chemical properties have already been given (p. 443). The metal unites with hydrogen to form a **hydride** NaH, which resembles potassium hydride (p. 444). The **amalgam** with mercury, when it contains more than a small amount of sodium, is solid, and contains one or more compounds of the two elements. This amalgam is often used instead of the metal sodium, since the dilution and combination with mercury make the interactions of the metal more easily controllable. Sodium is used in the manufacture of sodium peroxide and of many carbon compounds which are used as drugs and dyes.

Sodium Chloride NaCl.—Common salt is obtained from the salt deposits of Stassfurt and Reichenhall (near Salzburg), in Cheshire, at Syracuse and Warsaw in New York, at Salina in Kansas, in Utah, California, and many other districts. Natural brines are obtained from wells in various parts of the world. Since the salt can seldom be used directly, on account of impurities which it contains, it is purified by recrystallization from water. Natural brines, which are sometimes dilute, are often concentrated by dripping over extensive ricks composed of twigs. When the resulting brine is allowed to evaporate slowly by the help of the sun's heat, large crystals, sold as "solar salt," are obtained. By the use of artificial heat and stirring, smaller crystals of greater purity can be secured. In northern Russia, the brine is allowed to freeze, and the water thus removed in the form of ice (p. 134). Salt intended for table use must be freed from the traces of magnesium chloride (*q.v.*) present in the original brine or deposit, for this impurity causes it to absorb moisture more vigorously from the air. Addition of a little baking soda $NaHCO_3$ remedies the difficulty, by forming the insoluble magnesium carbonate. The purest salt for chemical purposes is precipitated from a saturated solution of salt by leading into it hydrogen chloride gas. Explanation of this effect will be given presently (see pp. 466–472).

Common salt crystallizes in cubes, the faces of which are usually hollow. The crystals decrepitate (p. 449) when heated, and melt at about 820°. Common salt is the source of all sodium compounds, with the exception of the nitrate. From it come also most of the chlorine and hydrogen chloride used in commerce. It is a necessary article of diet, furnishing, for example, the hydrochloric acid in the gastric juice (p. 147).

The Hydroxide and Oxides. — **Sodium hydroxide** NaOH, called also, colloquially, **caustic soda,** is prepared by the action of slaked lime upon sodium carbonate, but mainly by the electrolysis of a solution of sodium chloride, in both cases precisely as is potassium hydroxide (p. 446). Sodium hydroxide is a highly deliquescent substance. Its general chemical properties are identical with those of potassium hydroxide. It is used in the manufacture of soap, in the preparation of paper pulp, and in many other chemical industries.

Sodium peroxide Na_2O_2 is made by heating sodium at 300–400° in air which has been freed from carbon dioxide. The sodium is placed on trays of aluminium, and is passed into the furnace against the current of air. In this way, the freshest sodium meets the air from which most of the oxygen has been removed, and the action is moderated. Conversely, the almost entirely oxidized sodium meets the freshest air, and completion of the oxidation is thus assured.

This oxide is the sodium salt of hydrogen peroxide. When thrown into water it decomposes in part, in consequence of the heat developed, giving sodium hydroxide and oxygen. With careful cooling, however, much of it can be dissolved. By interaction with acids it yields hydrogen peroxide (p. 222). Sodium peroxide is now used commercially for oxidizing and bleaching, and, in the form of oxone (p. 28), as a source of oxygen.

The ordinary **sodium oxide** Na_2O is made in the same way as is potassium oxide (p. 447).

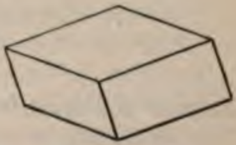


FIG. 115.

The Nitrate and Nitrite. — The occurrence and purification of **sodium nitrate** $NaNO_3$ have already been described (p. 347). Its crystals are of rhombohedral form (Fig. 115). This salt is one of the best of fertilizers, since it furnishes to plants the nitrogen which they require in a very easily absorbed form. It is used also in the manufacture of potassium nitrate, and of nitric acid.

Sodium nitrite $NaNO_2$ is formed by heating sodium nitrate with metallic lead and recrystallizing the product (p. 356).

Manufacture of Sodium Carbonate.—Natural sodium carbonate is found in Egypt and in other parts of the world. At Owen's Lake, California, it is secured by solar evaporation of the water. The sesquicarbonate $Na_2CO_3,NaHCO_3,2H_2O$, being the least soluble of the carbonates of sodium, is the one deposited. Locally, small quantities of sodium carbonate are still made by the burning of sea-weed. The substance is manufactured from sodium chloride in two ways, namely by the Le Blanc process and by the Solvay process. In 1900, however, only two factories used the former process.

The **Le Blanc process** (1791) involves three chemical actions. In the first place, sodium chloride is treated with an equivalent amount of sulphuric acid in a large cast-iron or earthenware pan. The bisulphate thus produced (*cf.* p. 141), together with the unchanged sodium chloride, is raked out on to the hearth of a reverberatory* furnace (Fig. 116), or into a rotating, inclined iron cylinder, and heated more strongly until the action is completed:

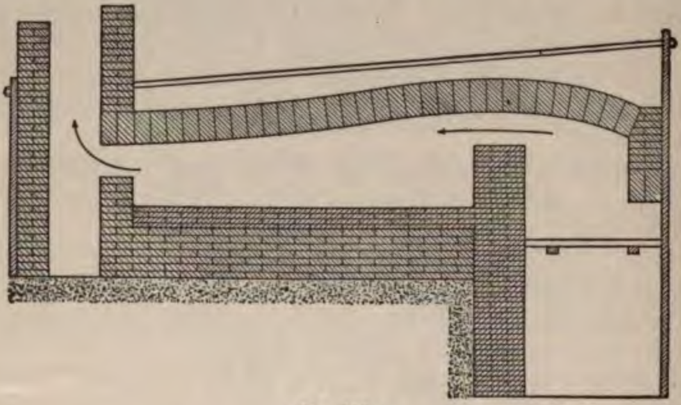


FIG. 116.

$$NaCl + NaHSO_4 \rightleftarrows Na_2SO_4 + HCl\uparrow.$$

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* So called because the heated gases from the fire are *deflected* by the roof and play upon the materials spread on the bed of the furnace.

The product of this treatment is called **salt cake.** The hydrogen chloride, which is liberated in both stages, passes through towers containing running water in which it is absorbed. The second and third actions which follow are conducted in one operation. They consist in the reduction of the sodium sulphate by means of powdered coal and the interaction of the resulting sulphide of sodium with chalk or powdered limestone, leaving finally **black ash**:

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2,$$
$$Na_2S + CaCO_3 \rightarrow Na_2CO_3 + CaS.$$

Calcium sulphide is not very soluble in water, and is but slowly hydrolyzed by it (p. 273), especially when calcium hydroxide is present. The sodium carbonate is therefore extracted from the black ash by a systematic treatment of the ash with water. The ash is placed in a series of vessels at different levels, and a stream of water (30–40°) flows from one vessel to another, until, when it issues from the last, it is completely saturated with sodium carbonate. When the material in the first of the vessels has been exhausted, the water is allowed to enter the second vessel directly, and a vessel containing fresh black ash is added at the lower end of the series. In this way the most nearly exhausted ash comes in contact with pure water, which is in the best position to dissolve the remaining sodium carbonate rapidly, while the fresh black ash encounters a solution already almost at the point of saturation. The commercial survival of the process depends upon the recovery of the sulphur from the spent black ash, and of the hydrogen chloride.

The **Solvay,** or **ammonia-soda process** (1860), has now displaced the Le Blanc process. It differs from the latter by involving almost nothing but ionic actions. A solution of salt, containing ammonia and warmed to 40°, fills a tower divided by a number of perforated partitions. Carbon dioxide, which is forced in below, makes its way up through the liquid. The ammonium bicarbonate formed by its action undergoes double decomposition with the salt, and sodium bicarbonate which is precipitated (sol'ty, 9.6 g. in 100 c.c. Aq) settles upon the partitions:

$$NaCl + NH_4HCO_3 \leftrightarrows NaHCO_3 \downarrow + NH_4Cl,$$

or

$$HCO_3^- + Na^+ \rightleftarrows NaHCO_3 \downarrow .$$

The solid sodium bicarbonate, after being freed from the liquid, is heated strongly and leaves behind sodium carbonate:

$$2NaHCO_3 \leftarrow Na_2CO_3 + H_2O\uparrow + CO_2\uparrow.$$

The carbon dioxide which is liberated passes through the operation once more. The supply of carbon dioxide is generated in lime-kilns of special form. The mother-liquor from the sodium bicarbonate contains ammonium chloride. This is decomposed by heating with quicklime from the kilns, and the ammonia which is thus obtained is available for the treatment of another batch.

The anhydrous sodium carbonate (**soda ash or calcined soda**) is recrystallized from water, giving the decahydrate $Na_2CO_3,10H_2O$, **soda crystals**, or **washing soda.** The bicarbonate is **baking soda.**

Properties of the Carbonate and Bicarbonate. — The common form of sodium carbonate consists of large monoclinic crystals of the **decahydrate** $Na_2CO_3,10H_2O$. This substance has a fairly high aqueous tension, and loses nine of the ten molecules of water which it contains when it is exposed in an open vessel (p. 96), leaving the monohydrate. When warmed it melts at 35.2°, giving a solution of sodium carbonate in water. The deposit from evaporation, above 35.2°, is the **monohydrate** Na_2CO_3,H_2O. At higher temperatures, or in a dry atmosphere (p. 96), this in turn can be completely dehydrated. In aqueous solution, sodium carbonate is hydrolyzed (2.3 per cent in $0.1N$ solution at 25°), and shows a marked alkaline reaction (p. 383). The compound is used in large amounts for the manufacture of glass and soap, and in the softening of water, and is applied in innumerable ways in the scientific industries for purposes akin to cleansing.

All the familiar compounds of sodium, excepting sodium nitrate and the peroxide, are made by the treatment of sodium carbonate or sodium hydroxide with acids.

Sodium bicarbonate $NaHCO_3$ is formed in the Solvay process (p. 461). It can be prepared in a state of purity by passing carbon dioxide over the decahydrate of sodium carbonate:

$$Na_2CO_3,10H_2O + CO_2 \rightleftarrows 2NaHCO_3 + 9H_2O.$$

This action is reversible (*cf.* p. 384), and sodium bicarbonate shows, even in the cold, an appreciable tension of carbon dioxide. The aqueous solution of the *pure* substance is neutral to phenolphthaleïn, on account of the small degree of ionization of the ion HCO_3^-. Ordinarily, however, the solution is alkaline, on account of the presence of the carbonate, which is hydrolyzed. The salt is used in the manufacture of baking powder and in medicine.

Baking Powders. — The object of using the powder is to generate carbon dioxide in the dough. The bubbles are retained because of the presence of the sticky gluten, a protein (p. 3). They expand when the dough is heated in baking, and give to the bread its porous texture.

Baking soda, alone, will give off carbon dioxide, but the sodium carbonate which it leaves behind has a disagreeable taste and acts upon the gluten causing a yellow color and unpleasant smell. It also tends to neutralize the acid in the gastric juice and so impedes digestion. To prevent this result, sour milk (containing lactic acid) and even vinegar are added. Usually, however, a **baking powder** containing an acid substance along with the bicarbonate is employed. Potassium bitartrate (**cream of tartar**) $KHC_4H_4O_6$ (p. 452) is most commonly employed, although alum and primary sodium or ammonium orthophosphate (p. 370) are also used:

$$HKC_4H_4O_6 + NaHCO_3 \rightarrow NaKC_4H_4O_6 + H_2CO_3 \rightarrow H_2O + CO_2.$$

The cream of tartar has the advantages that it is somewhat insoluble and does not act noticeably upon the soda before the mixing of the dough is complete, and that the sodium-potassium tartrate (**Rochelle Salts**) produced is not harmful. A little starch is added to baking powders to keep the particles of the two other ingredients apart, and prevent gradual interaction before use.

For raising bakers' bread, yeast is employed, and time is allowed for the propagation of the yeast and its action upon the sugar (p. 406) in the flour. A little molasses or malt extract is often added, to ensure a sufficient supply of sugar.

The whites of eggs cause cake to rise, largely because they are whipped before use, and bubbles of air, which expand when heated, are thus introduced.

Other Salts of Sodium. — **Anhydrous sodium sulphate** Na_2SO_4 (thenardite) is found in the salt layers. The same salt is contained in mineral waters, such as those of Friedrichshall and Karlsbad. It is formed in connection with the manufacture of nitric acid from sodium nitrate. It is used, as a substitute for sodium carbonate, in making inexpensive glass.

The **decahydrate of sodium sulphate** $Na_2SO_4,10H_2O$ (**Glauber's salt**) forms large monoclinic crystals which give up all their water of hydration when kept in an open vessel. When heated, the crystals melt at 32.4°, giving the sulphate and water. For the solubilities of the hydrate and anhydrous substance, see Fig. 59 (p. 132).

Sodium thiosulphate $Na_2S_2O_3,5H_2O$, formerly called hyposulphite of soda, and still called **hypo** by photographers, is made by boiling a solution of sodium sulphite with sulphur (p. 290). A standard solution (p. 257) of the thiosulphate is used in determining quantities of free iodine:

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6.$$

Colorless **sodium tetrathionate** is formed, and the "end point" (consumption of all the iodine) can be ascertained by the starch test (see p. 480).

When heated, dry sodium thiosulphate first loses the water of hydration, and then decomposes, giving sodium sulphate, which is the most stable oxygen-sulphur compound of sodium (*cf.* p. 290) and sodium pentasulphide:

$$4Na_2S_2O_3 \rightarrow 3Na_2SO_4 + Na_2S_5.$$

From the latter, four unit-weights of sulphur can be driven by stronger heating. Sodium thiosulphate is used for fixing negatives in photography (*q.v.*), and by bleachers as an antichlor.

Sodium hyposulphite $\mathbf{Na_2S_2O_4}$ is prepared in solution by the action of zinc on sodium bisulphite and excess of sulphurous acid:

$$Zn + 2NaHSO_3 + H_2SO_3 \rightarrow Na_2S_2O_4 + ZnSO_3 + 2H_2O.$$

The solution is an active reducing agent, and is employed largely by dyers, for example in reducing indigo (insoluble) to indigo white (soluble in an alkaline liquid), in preparing the vat of dye.

Common **sodium phosphate** is a dodecahydrate of the secondary orthophosphate, $Na_2HPO_4,12H_2O$. It is made by neutralization of phosphoric acid with sodium carbonate. Its properties have already been discussed (pp. 370–371).

Sodium metaphosphate $NaPO_3$ is formed in bead tests (p. 371).

Sodium tetraborate $Na_2B_4O_7,10H_2O$ (**borax**) forms large, transparent prisms. When heated it loses water, and leaves the easily fusible anhydrous salt in glassy form. Its sources have already been discussed under borates (p. 432). It is used as an ingredient in glazes for porcelain, in soldering, for bead reactions (p. 433) and for preserving food.

Sodium disilicate $Na_2Si_2O_5$ (*cf.* p. 428) is used for fireproofing wood and other materials, and for preserving eggs. Sand which is moistened with it and pressed in molds, forms, after baking, a serviceable artificial stone.

For **sodium cyanide,** see p. 488.

Properties of Sodium-ion Na^+: Analytical Reactions. — Sodium-ion is a colorless ionic material which unites with all negative ions. Practically all the salts so formed are soluble in water. The only ones which can be precipitated are sodium fluosilicate Na_2SiF_6, made by the addition of hydrofluosilicic acid to a strong solution of a sodium salt, and sodium-hydrogen pyroantimoniate $Na_2H_2Sb_2O_7$, made by similar addition of the corresponding potassium salt. All compounds of sodium confer a yellow color on the Bunsen flame, but this test is so delicate that it is shown by the traces of sodium contained in almost all substances.

Lithium. — Lithium occurs in lepidolite (a lithia mica), in amblygonite, and in other rare minerals. Traces of compounds of the element are found widely diffused in the soil, and are taken up by plants, particularly tobacco and beets, in the ashes of which the element may be detected spectroscopically.

The metal is liberated by electrolysis of the fused chloride. The specific gravity of the free element (0.53) is lower than that of any other metal. Lithium not only floats upon water, but also in the petroleum in which it is preserved.

The metal behaves towards water and oxygen like sodium (p. 50). It unites directly and vigorously with hydrogen (LiH), nitrogen (Li_3N), and oxygen (Li_2O), forming stable compounds. The relative insolubility (see Table) of the hydroxide LiOH, the carbonate Li_2CO_3, and the phosphate $Li_3PO_4,2H_2O$ is in sharp contrast to the easy solubility of the corresponding compounds of the other alkali-metals, and links lithium with magnesium. The compounds of lithium give a bright-red color to the Bunsen flame. A bright-red and a somewhat less bright orange line are seen in the spectrum. The carbonate is used in medicine.

IONIC EQUILIBRIUM, CONSIDERED QUANTITATIVELY

In view of the predominance of ionic actions in the chemistry of the metals, and of the determinative effect of ionic equilibria on many actions, it is essential that we should be prepared in future for a more exact consideration of these phenomena than we have hitherto attempted. The whole *basis* for this exact consideration *has already been supplied*, and only more specific application of the principles is demanded. The basis referred to, which should now be re-read as a preliminary to what follows, is contained in, (1) the discussion of chemical equilibrium in general (pp. 177–190), (2) the application of the same principles to ionic equilibrium (p. 238), and (3) the illustration of this application in the case of cupric bromide (pp. 246–251).

Excess of One Ion. — In the case of cupric bromide, we showed that increasing the concentration of the bromide ions displaced the equilibrium by favoring the union of the ions to form molecular cupric bromide: $2Br^- + Cu^{++} \rightarrow CuBr_2$. This we speak of as a **repression of the ionization** of the cupric bromide. Now, if the substance is a *slightly* ionized one, like a weak acid or a weak base, the repression of the ionization through the formation of molecules in this way may remove so many of that one of the ions which is not present in excess (corresponding to the Cu^{++} in the foregoing illustration), that the mixture will no longer respond to tests for the ion so removed. This is an interesting and very common case. The behavior of acetic acid, a weak, slightly ionized acid, will serve as an illustration.

In normal solution (60 g. in 1 l.) acetic acid is only 0.004 ionized (p. 241), so that, in the equation for the equilibrium,

$$(0.996)\ HC_2H_3O_2 \leftrightarrows H^+\ (0.004) + C_2H_3O_2^-\ (0.004),$$

the relative proportions are as shown by the numbers in parenthesis. If the whole of the acid (60 g.) were ionized, there would be 1 g. of hydrogen-ion per liter. Yet, even in the much smaller concentration actually present (0.004 g. per liter), the acid taste of the H^+ and its effect upon indicators can be distinctly recognized. If, *now*, solid sodium acetate is dissolved in the solution, the liquid *no longer gives an acid reaction* with one of the less delicate indicators, like methyl orange (p. 258). The explanation is simple. Sodium acetate is highly ionized. It gives, therefore, a large concentration of acetate-ion to a liquid formerly containing very little. This causes a greatly increased union of the H^+ ions and $C_2H_3O_2^-$ ions to occur, and the former, being already very few in number, disappear almost entirely. Hence the solution becomes, to all intents and purposes, neutral. There is no less *acetic acid* present than before, but the concentration of hydrogen-ion is very much smaller.

Formulation and Quantitative Treatment of the Case of Excess of One Ion. — If the semi-mathematical mode of formulating an equilibrium (p. 184), as applied to the case of an ionogen (p. 238), be employed here, the foregoing general statements may be made more precise and the conclusions clearer. If $[H^+]$ and $[C_2H_3O_2^-]$ represent the *molecular concentrations* of hydrogen-ion and acetate-ion, respectively, and $[HC_2H_3O_2]$ that of the acetic molecules at equilibrium, then:

$$\frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = K.$$

The value of K is constant, whether the strength of the solution of acetic acid is great or small, and even when another substance with a common ion is present. In the latter case, $[C_2H_3O_2^-]$ and $[H^+]$ stand for the *whole* concentrations of each of these ionic substances from *both* sources.

Now, in normal acetic acid $[H^+] = 0.004$, $[C_2H_3O_2^-] = 0.004$ (for the number of each kind of ions is the same), and $[HC_2H_3O_2] = 0.996$, practically 1. Substituting in the formula:

$$\frac{0.004 \times 0.004}{1} = K\ (= 0.0_4 16).$$

When, however, sodium acetate is dissolved in the liquid until the solution is normal in respect to this substance *also*, the following additional equilibrium has to be considered:

$$(0.47)\ NaC_2H_3O_2 \rightleftarrows Na^+\ (0.53) + C_2H_3O_2^-\ (0.53).$$

The concentration of acetate-ion from this source is 0.53, so that, in the mixture of acid and salt, the concentration of acetate-ion $[C_2H_3O_2^-]$ will be $0.53 + 0.004 = 0.534$, or nearly 134 times larger than in the acid alone. Hence, in order that the product $[H^+] \times [C_2H_3O_2^-]$ may recover, as it must, a value much nearer to the old one, $[H^+]$ must be diminished to something like $\frac{1}{134}$ of its former magnitude. That is, $[H^+]$ will become equal to about 0.00003,

$$\frac{0.00003 \times 0.534}{1} = K\ (= 0.0_416),$$

the rest of the hydrogen-ion uniting with a corresponding amount of the acetate-ion to form molecular acetic acid. The effect of adding this amount of sodium acetate therefore is, as we have seen, to reduce the concentration of the *hydrogen-ion* below the amount which can be detected by use of an indicator like methyl orange.

This effect is of course reciprocal, and the ionization of the sodium acetate will be reduced also. But the acetate-ion furnished by the acetic acid is relatively so small in amount (0.00003 against 0.53) that the effect it produces on the ionization of the salt is imperceptible.

It will be noted that the acetate-ion and hydrogen-ion disappear in equivalent quantities, for they unite. There is, however, so much of the former that the loss it sustains goes unremarked, while there is so little of the latter that almost none of it remains. When substances of more nearly equal degrees of ionization are used, *both effects are equally inconspicuous.* Thus, sodium chloride and hydrogen chloride in normal solutions yield approximately equal concentrations of chloride-ion (0.784 and 0.66). Hence, if one mole of sodium chloride were to be dissolved in the portion of water already containing one mole of hydrogen chloride, the concentration of the chloride-ion, at a very rough estimate, would be nearly doubled. If this doubling of the concentration of chloride-ion almost halved that of the hydrogen-ion (0.784), in order that the expression $[Cl^-] \times [H^+] \div [HCl]$ might remain constant, the concentration of the hydrogen-ion would still be about 0.400 and therefore 100 times as great as in molar acetic acid. It is thus altogether impossible to reduce the concentration of the hydrogen-ion given by an *active* acid like hydrochloric acid below the limit at which indicators are affected, for there is no way of introducing the enormous concentration of the other ion which the theory demands.

With more crude means of observation than indicators afford, effects like this last may sometimes be rendered visible. This was the case with cupric bromide solution, to which potassium bromide was added (p. 250). The blue of the cupric-ion disappeared from view, while much cupric-ion was still present, because the brown color of the molecular cupric bromide covered it up completely.

Special Case of Saturated Solutions. — The commonest as well as the most interesting application of the conceptions developed above is met with in connection with saturated solutions, especially those of relatively insoluble substances.

The situation in a system consisting of the saturated solution and excess of the solute has been discussed already (read p. 127). In the case of potassium chlorate, for example, we have the following scheme of equilibria:

$$KClO_3 \text{ (solid)} \rightleftarrows KClO_3 \text{ (dslvd)} \rightleftarrows K^+ + ClO_3^-.$$

Solution of the solid is promoted by the solution pressure of the molecules, while it is opposed by the osmotic pressure of the dissolved substance, and the solution is saturated when these tendencies produce equal effects (p. 128). Now it must be noted that the tendency *directly* opposed to the solution pressure is the *partial* osmotic pressure of the dissolved *molecules* alone. The chief contents of the solution, the molecules and two kinds of ions of the salt, and any foreign material that may be present, are like a mixture of gases, and the principle of partial pressure (p. 72) is to be applied. The ions and the foreign material do not deposit themselves upon the solid, and take, therefore, no part *directly* in the equilibrium which controls solubility. In respect to this the ions are themselves foreign substances. Hence the conclusion may be stated that, **in solutions saturated at a given temperature by a given solute, the concentration of the dissolved molecules of the solute considered by themselves will be constant whatever other substances may be present.**

The total "solubility" of a substance, as we have used the term hitherto, is made up of a molecular and an ionic part. The latter, as we shall presently see, is not constant when a foreign substance containing a common ion is already in the liquid. Since the treatment of the subject requires us now to distinguish between the two portions of the solute, a diagram (Fig. 117) will assist in emphasizing the distinction. The material at the bottom is the salt. The molecules and ions are to be thought of as being mixed and as being present in numbers represented by the factors *n* and *m*. Since no foreign body is present, the two ions in this case are equal in number.

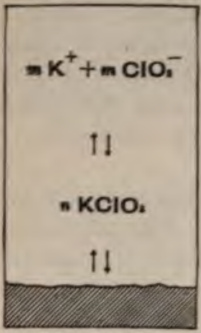

Fig. 117.

When we now apply these ideas to the mathematical expression of the relation:

$$\frac{[K^+] \times [ClO_3^-]}{[KClO_3]} = K$$

we perceive that, in a *saturated* solution, $[KClO_3]$, the concentration of the molecules, is *constant*. Transposing, we have

$$[K^+] \times [ClO_3^-] = K[KClO_3] = K'.$$

Hence the relation leads to the important conclusion that, **in a saturated solution, the product of the molar concentrations of the ions is constant.*** This product is called the **ion-product constant** for the substance. The **law** of the constancy of the ion-product in a saturated solution is one of the most useful of the principles of chemistry. It enables us to explain all the varied phenomena of precipitation and of the solution of precipitates in a consistent manner. These applications of the principle will be explained in the next chapter. One curious kind of precipitation will be described here, however, as an illustration of the use of the principle.

Illustration of the Principle of Ion-Product Constancy. — When, to a *saturated* solution of one of the less soluble salts, a strong solution of a very soluble salt having *one ion in common* with the first salt is added, precipitation of the first salt frequently takes place. This happens, for example, with a saturated solution of potassium chlorate, which is not very soluble (molar solubility 0.52, see Table). The concentrations $[K^+]$ and $[ClO_3^-]$ being small, one may easily increase the value for one of the ions, say $[ClO_3^-]$, fivefold, by adding a chlorate which is sufficiently soluble. To preserve the value of the product $[K^+] \times [ClO_3^-]$, the value of $[K^+]$ will then have to be diminished at once to one-fifth of its former value. This can occur only by union of the ionic material it represents with an equivalent amount of that for which $[ClO_3^-]$ stands. The molecular material so produced will thus tend at first to swell the value of $[KClO_3]$. But the value of $[KClO_3]$ cannot be increased, for the solution *is already saturated with molecules*, so that the **new supply of molecules,** or others in equal numbers, **will be precipitated.** Hence the ionic part of the dissolved substance may be diminished, the equilibria (p. 469) may be partially reversed, and we may actually precipitate a part of the dissolved material without introducing any substance, which, in the ordinary sense, can interact with it.

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* The principle of constant concentration of dissolved molecules, stated above, has been shown to express the facts very inaccurately. Now the principle of the constancy of the ratio of the ion-product to the concentration of the molecules is also inaccurate in the case of highly ionized substances, yet in such a way that the two errors neutralize one another. Thus, the principle of ion-product constancy here given is in itself fairly exact.

In point of fact, when, to a saturated solution of potassium chlorate there is added a saturated solution of potassium chloride KCl (molar solubility, 3.9) or of sodium chlorate $NaClO_3$ (molar solubility, 6.4), a precipitate of potassium chlorate is thrown down. These two salts, each containing one of the ions of $KClO_3$, and being much more soluble than the latter (see Table), increase the concentration of one ion and cause the precipitation in the fashion just explained.

The product of the concentrations of the ions, for example $[K^+] \times [ClO_3^-]$, is called also the **solubility product,** because these two values jointly determine the magnitude of the solubility of the substance. The solubility of the molecules is irreducible, but the ionic part of the dissolved material may become vanishingly small if the value of either $[X^+]$ or $[Y^-]$ is very minute. The ionic part of any particular substance is made up of the smaller of the two concentrations of the ionic substances which it yields, plus an equivalent amount, and no more, of the concentration of the other ion. The rest of the other ionic substance is part of the solubility of some other component.

Other Illustrations. — The precipitation of sodium chloride from a saturated solution, by the introduction of gaseous hydrogen chloride (p. 458), is to be explained in the same manner. The equilibria:

$$\text{NaCl (solid)} \rightleftarrows \text{NaCl (dslvd)} \rightleftarrows \text{Na}^+ + \text{Cl}^-$$

are reversed by the introduction of additional Cl^- from the very soluble, and highly ionized HCl.

A steady stream of hydrogen chloride is often obtained by dropping concentrated sulphuric acid into saturated hydrochloric acid:

$$\text{H}^+ + \text{Cl}^- \rightleftarrows \text{HCl (dslvd)} \rightleftarrows \text{HCl (gas)}.$$

The effect is due in part to repression of the ionization of the hydrogen chloride and elimination of molecules of the gas from the water which is already saturated with molecules of the same kind.

The formation of potassium hydroxide (p. 446) ceases when a certain concentration has been reached. This occurs because the concentration of OH^-, which rapidly increases, is a factor in the solubility product of calcium hydroxide, $[Ca^{++}] \times [OH^-]^2$. With much OH^-, little Ca^{++} is required to give the constant, numerical value of the product. When the concentration $[Ca^{++}]$ from the hydroxide has become about as small as that from the carbonate, the motive for the interaction has been removed. This principle is thus as important in industrial operations as it is in analytical and other laboratory experimentation.

Exercises. — 1. The vapor density of sodium peroxide has not been determined. Why is the formula Na_2O_2 assigned to it?

2. Construct a scheme of equilibria (p. 271) showing the hydrolysis of calcium sulphide. Why does the presence of calcium hydroxide diminish the tendency to hydrolysis (p. 461)?

3. What will be the effect of adding a concentrated solution of silver nitrate to a saturated solution of silver sulphate (see Table of solubilities)?

4. Although a 20 per cent solution of soap can easily be made, a 0.5 per cent solution can be salted out (p. 417). How does this fact show that salting out is *not* an operation like the precipitations just discussed?

CHAPTER XXXVI

THE METALLIC ELEMENTS OF THE ALKALINE EARTHS

The Chemical Relations of the Elements. — The familiar metals of this group, **calcium** (Ca, at. wt. 40.1), **strontium** (Sr, at. wt. 87.6), and **barium** (Ba, at. wt. 137.4), constitute a typical chemical family, both in the qualitative resemblance to one another of the elements and of the corresponding compounds, and in the quantitative variation in the properties with increasing atomic weight. The metals themselves displace hydrogen vigorously from cold water, giving hydroxides. The solutions of these hydroxides, although dilute, on account of a rather small solubility, are strongly alkaline in reaction. The high degree of ionization of the hydroxides recalls the hydroxides of the metals of the alkalies, and their relative insolubility the hydroxides of the "earths" (*q.v.*).

In all their compounds, calcium, strontium, and barium are bivalent. The hydroxides are formed by union of the oxides with water, and are progressively less easy to decompose by heating, barium hydroxide being the hardest. The carbonates, when heated, yield the oxide of the metal and carbon dioxide, barium carbonate being the most difficult to decompose. The nitrates, when heated moderately, give the nitrites, but the latter are broken up by further heating and yield the oxide of the metal, and nitrogen tetroxide. In these and other respects the compounds of the metals of the alkaline earths resemble those of the heavy metals and differ from those of the metals of the alkalies. Barium approaches the latter most nearly.

The table of solubilities (*q.v.*) shows that the chlorides and nitrates of calcium, strontium, and barium are all soluble in water, the solubility diminishing in the order given. The sulphates and hydroxides cover a wide range from slight solubility to extreme insolubility. Of the sulphates, 2100, 110, and 2.3 parts, respectively, dissolve in one million parts of water. In the case of the hydroxides the order of magnitude is reversed, and the corresponding numbers are 200, 630, and 2200. The carbonates are almost as insoluble as is barium sulphate. Radium (Ra, at. wt. 226) belongs to this family (see under Uranium).

CALCIUM Ca

Occurrence. — The fluoride, and the various forms of the carbonate, sulphate, and phosphate, which are found in nature, are described below. As silicate, calcium occurs, along with other metals, in many minerals and rocks. Compounds of the element are found also in plants, and in the bones and shells of animals.

The Metal. — Calcium is made by electrolysis of the molten chloride. A hollow cylinder made of blocks of carbon bolted together and open above, forms the anode. A rod of copper hanging so that its end dips into the melt forms the cathode. The melting of the anhydrous calcium chloride with which the cylinder is filled is started by means of a thin rod of carbon laid across from the anode to the cathode. When the heat generated by the passage of the current through this highly resisting medium has melted a sufficient amount of the salt, the rod is removed, and the resistance of the fused material suffices to maintain the temperature. The calcium rises round the cathode and collects on the surface of the bath. By slowly elevating the copper cathode, the calcium, which adheres to it, may be drawn out of the fused mass in the form of a gradually lengthening, irregular rod. The rod of calcium is kept constantly in contact with the metal which accumulates on the surface, and thus forms one of the electrodes.

Calcium is a silver-white, crystalline metal (m.-p. 800°, sp. gr. 1.55) which is a little harder than lead, and can be cut, drawn, and rolled. It interacts rapidly with water. When heated it unites vigorously with hydrogen, oxygen, the halogens, and nitrogen. On this account it is used in producing a high degree of evacuation. It burns in the air, giving a mixture of the oxide and **nitride** Ca_3N_2. The presence of the latter may be shown by the liberation of ammonia when water is added to the residue:

$$Ca_3N_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2NH_3.$$

A white crystalline **hydride** CaH_2 is formed by direct union of the constituents. It is known in commerce as **hydrolyte.** It is an expensive, but portable source of hydrogen for filling war balloons:

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2.$$

Calcium Chloride $CaCl_2$. — This salt, for which there is no extensive commercial application, is formed as a by-product in many industrial operations. Thus, it is a by-product of the Solvay soda process (p. 461). By evaporation of any solution, the **hexahydrate** $CaCl_2,6H_2O$ is obtained in large, deliquescent, six-sided prisms. On account of the great concentration of a saturated solution of this compound, the solid and solution do not reach a condition of equilibrium with ice (*cf.* p. 134) until the temperature has fallen below −50°. The Solvay process brine (p. 462) when mixed with ice, gives, therefore, a very efficient freezing mixture. On account of its deliquescent character, the solid salt is sprinkled on roads to lay the dust.

Calcium chloride, partly **dehydrated** by heating, $CaCl_2,2H_2O$, forms a porous mass which is used in chemical laboratories for drying gases and liquids. When complete dehydration is attempted, the salt interacts with the water, giving some calcium oxide.

Calcium chloride forms compounds, not only with water, but also with ammonia ($CaCl_2,8NH_3$) and with alcohol. For drying these substances, therefore, quicklime is employed.

Calcium Fluoride CaF_2. — This compound occurs in nature as fluorite or fluor-spar CaF_2. It crystallizes in cubes, is insoluble in water, and when pure is colorless. Natural specimens often possess a green tint or show a violet fluorescence. It is formed as a precipitate when a soluble fluoride is added to a solution of a salt of calcium.

Fluorite is used in the etching of glass, as the source of the hydrogen fluoride (p. 205). It is easily fusible, as its name indicates (Lat. *fluere*, to flow), and is employed in metallurgical operations as a flux (p. 438), for lowering the melting-point (or freezing-point, which is the same thing, *cf.* p. 134) of the slag (p. 438), and so facilitating the separation of the latter from the metal.

Calcium Carbonate $CaCO_3$.—This compound is found very plentifully in nature. Limestone is a compact, indistinctly crystalline variety, while marble is a distinctly crystalline form. Chalk* is a deposit consisting of the calcareous parts of minute organisms. Egg-shells, oyster-shells, coral, and pearls are other varieties of organic origin.† Calcite and Iceland spar (Ger. *spalten*, to split) are pure crystallized calcium carbonate. The former occurs in flat rhombohedrons, or in pointed, six-sided crystals (Fig. 43, p. 83) (scalenohedrons) of "dog-tooth" spar, belonging to the same system.

When heated, calcium carbonate dissociates, giving carbon dioxide and quicklime:

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

At ordinary temperatures the decomposition is imperceptible. On the contrary, atmospheric carbon dioxide, in spite of its very low partial pressure, combines with quicklime, giving "air-slaked" lime. As the temperature rises, however, **the tension of carbon dioxide** coming from the carbonate increases, and **has a fixed value for each temperature.** If it is continuously allowed to escape, so that the maximum pressure is not reached, the whole of the salt eventually decomposes. At 700° the pressure is only 25 mm., at 900° it reaches an atmosphere, and at 950° two atmospheres. The phenomenon is precisely similar to the dissociation of a hydrate (p. 96) and to the evaporation of a liquid (p. 88).

Limestone is soluble in water containing carbonic acid, giving calcium bicarbonate (p. 384, also see p. 489). By solution of limestone, caves are often formed. Conversely, subterranean water containing the bicarbonate, when it reaches such a cavern, loses carbon dioxide and deposits calcium carbonate as **stalactites** or columns hanging from the ceiling. The drippings form **stalagmites** on the floors.

Limestone is used in the manufacture of quicklime (*q.v.*) and of glass. It is employed largely as a flux in metallurgy, when minerals rich in silica are brought into fusible form by the production of calcium silicate $CaSiO_3$. Large amounts also find application as building-stone.

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* Blackboard "crayon" is usually made of gypsum and not of chalk.

† The hard coverings of crustacea and insects are not made of this substance, but of an organic material called **chitin.**

Calcium Oxide and Hydroxide. — Pure **oxide of calcium** CaO (**quicklime**) may be made by ignition of pure marble or calcite. For commercial purposes limestone is converted into quicklime in kilns (Fig. 118). The flames and heated gases from the fire pass between the pieces of limestone, and the carbon dioxide liberated is carried off by the draft. When the gas is to be used in the Solvay process or in the refining of sugar, coke (smokeless), instead of coal, is employed as the fuel. As low a temperature as possible is used. A high temperature causes impurities in the limestone (*e.g.*, clay) to interact with the quicklime, giving fusible silicates, which fill the pores and interfere with the subsequent slaking with water. Since the change is reversible, if the gas lingers in the kiln (at 760 mm. pressure), a temperature over 900° is required to drive the action forward (p. 476). Hence, a good draft, which removes the gas as fast as it is formed, permits the use of a lower temperature.

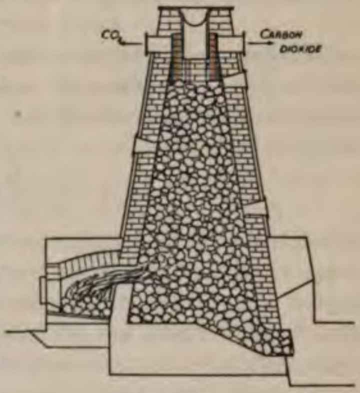

FIG. 118.

Pure calcium oxide is a white, porous solid. It is barely fusible in the oxyhydrogen flame, but may be melted and boiled in the electric arc. It is not reducible by sodium, or by carbon excepting at the temperature of the electric furnace.

When water is poured upon quicklime, it is first absorbed into the pores mechanically, and then unites chemically to form **calcium hydroxide** $Ca(OH)_2$:

$$CaO + H_2O \leftrightarrows Ca(OH)_2.$$

The product is a bulky powder. Much heat is evolved, and part of the water is turned into steam. The change is reversible, and at a high temperature the hydroxide can be dehydrated.

Calcium hydroxide is slightly soluble in water: 1 part in 600 parts of water at 18°, about twice as much water being required at 100°. The solution, relatively to its concentration, is strongly alkaline. On account of its cheapness, this substance is use manufacturers in almost all operations requiring a base, and it thus occupies the same position amongst bases that sulphuric acid does amongst acids. Caustic lime is employed in the manufacture of alkalies (p. 446), bleaching powder, and mortar (see below), the removal of the hair from hides in preparation for tanning, the softening of water (see below) and as a whitewash.

Mortar. — Mortar is made by mixing water with slaked lime and a large proportion of sand. The "hardening" process consists in an interaction of the carbon dioxide of the air with the calcium hydroxide:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O.$$

After the superficial parts have been changed, the process goes on very slowly, and many years are required before the deeper layers have been transformed. The minute crystals of calcite which are formed are interlaced with the sand particles, and a rigid, yet porous mass is produced. The "hardening" does not begin until the excess of water used in making the mortar has evaporated, and hence ordinary mortar is unsuitable for use in damp places such as cellars.

Calcium Oxalate CaC_2O_4. — This salt may be observed under the microscope in the cells of many plants. It appears in the form of needle-shaped or of granular crystals. Since it is the least soluble salt of calcium, its formation by precipitation is used as a test for calcium ions.

Theory of Precipitation. — The precipitation of calcium oxalate CaC_2O_4, just referred to, is a typical one and may be used to illustrate the application of ion-product constancy (p. 470) to explaining the phenomenon. The same explanation serves for all precipitations of ionogens.

The first thing to be remembered is that the precipitate which we observe, however insoluble its material may be, does not include *all* of the substance, but only the excess beyond what is required to saturate the water. **The liquid surrounding the precipitate is always a saturated solution of the substance precipitated.** If it were not so, some of the precipitate would dissolve until the liquid became saturated. Thus, for example, when we add ammonium oxalate solution to calcium chloride solution:

$$\left.\begin{array}{r}(NH_4)_2C_2O_4 \leftrightarrows 2NH_4^+ + C_2O_4^= \\ CaCl_2 \leftrightarrows 2Cl^- + Ca^{++}\end{array}\right\} \leftrightarrows CaC_2O_4\,(\text{dslvd}) \leftrightarrows CaC_2O_4\,(\text{solid}),$$

the liquid is a saturated solution of calcium oxalate, with the excess of this salt suspended in it as a precipitate.

Looking at the matter from this view point, we perceive the application of the rule of ion-product constancy. In this *saturated* solution (p. 470) the product of the ion-concentrations, $[Ca^{++}] \times [C_2O_4^=]$, is constant. If the original solutions had been so very dilute that, when they were mixed, the product of the concentrations of these two ions had *not* reached the value of this constant, *no precipitation would have occurred.* As a matter of fact the ion-product considerably exceeded the requisite value, and hence the salt was thrown down until the balance remaining gave the value in question. The **rule for precipitation,** then, is as follows: **Whenever the product of the concentrations of any two ions in a mixture exceeds the value of the ion-product in a saturated solution of the compound formed by their union, this compound will be precipitated.** Naturally the substances with small solubilities, and therefore small ion-product constants, are the ones most frequently formed as precipitates.

In the case of calcium oxalate, the molar solubility (see Table) is 0.0_443. In so dilute a solution the substance, being a salt (p. 242), must be practically all ionized. *Each* molecule gives one ion of each kind. The molar concentrations of these ionic substances, Ca^{++} and $C_2O_4^=$, *in the solution*, when the *solid is also present*, must therefore be (practically) 0.0_443, *each.* The product $[Ca^{++}] \times [C_2O_4^=]$ is thus equal to $0.0_443 \times 0.0_443$ or 0.0_8185. If in mixing the solutions, exactly equivalent quantities were not employed, the values of the two factors will not be equal, but the *product* will in any case possess this value.

Rule for Solution of Substances. — The **rule for solution** of *any* ionogen follows at once from the foregoing considerations, and may be formulated by changing a few of the words in the rule just given: **Whenever the *product* of the concentrations of any two ions in a mixture *is less than* the value of the ion-product in a**

saturated solution of the compound formed by their union, this compound, if present in the solid form, **will be *dissolved.*** When applied to the simplest case, this rule means that a substance will dissolve in a liquid not yet saturated with it, but will not dissolve in a liquid already saturated with the same material. The value of the rule lies in its application to the less simple, but equally common cases, such as when an insoluble body is dissolved by interaction with another substance (next section).

Applications of the Rule for Solution to the Solution of Insoluble Substances. — So long as a substance remains in pure water its solubility is fixed. Thus, with calcium hydroxide, the system comes to equilibrium at 18° when 0.17 g. per 100 c.c. of water (0.02 moles per liter) have gone into solution:

$$Ca(OH)_2 \text{ (solid)} \leftrightarrows Ca(OH)_2 \text{ (dslvd)} \leftrightarrows Ca^{++} + 2OH^{-}.$$

But if an additional reagent which can combine with either one of the ions is added, the concentration of this ion at once becomes less, the actual numerical value of the ion-product therefore begins to diminish, and further solution must take place to restore its value. Thus, if a little of an acid (giving H^+) be added to the solution of calcium hydroxide, the union of OH^- and H^+ to form water removes the OH^-, and solution of the hydroxide proceeds until the acid is used up. There are now more Ca^{++} than OH^- ions present, but the *ion-product* reaches the same value as before, and then the change ceases. If a further supply of acid is added, the removal of OH^- to form H_2O begins again. With *excess of the acid,* the only stable OH^- concentration is that which is a factor in the very minute ion-product of water, $[OH^-] \times [H^+]$, which is $0.0_61 \times 0.0_61$, or $0.0_{13}1$. Hence, with excess of acid, the calcium hydroxide, which requires in general a much higher concentration of OH^- than this to precipitate it or to keep it out of solution, finally all dissolves.

More specifically, if we assume that the calcium hydroxide is wholly dissociated in so dilute a solution (which is nearly true), each molecule forms one ion of Ca^{++} and two ions of OH^-. That is, each mole of $Ca(OH)_2$ gives one mole of Ca^{++} and two moles of OH^-. As the saturated solution contains 0.02 moles of the base, the molar concentration (assuming complete dissociation) of $[Ca^{++}]$ is 0.02 and of $[OH^-]$ is 0.04. Now, the ion-product is the product of the concentrations of all the ions formed, *i.e.* Ca^{++}, OH^-, and OH^-. The value of the product is therefore $[Ca^{++}] \times [OH^-] \times [OH^-]$ or $[Ca^{++}] \times [OH^-]^2$. That is, $0.02 \times 0.04^2 = 0.0_{4}32$. Note that if the molecule gives two (or three) ions of the same kind, the *whole* concentration of that ion is taken, and is also raised to the *second* (or third) *power*.

This particular action is a neutralization of an insoluble base. But the other kinds of actions by which insoluble ionogens pass into solution all resemble it closely, and differ only in details. The general outlines of the explanation are the same in every case. We proceed now to apply it to the common phenomenon of the solution of an insoluble salt by an acid.

Interaction of Insoluble Salts with Acids, Resulting in Solution of the Salt. — Calcium oxalate passes into solution when in contact with acids, especially active acids. Thus, with hydrochloric acid, it gives calcium chloride and oxalic acid, both of which are soluble:

$$CaC_2O_4\uparrow + 2HCl \leftrightarrows CaCl_2 + H_2C_2O_4. \tag{1}$$

The action of acids upon insoluble salts is so frequently mentioned in chemistry and is so important a factor in analytical operations that it demands separate discussion. This example is a typical one and may be used as an illustration.

According to the rules already explained (p. 479), calcium oxalate (or any other salt) is precipitated when the numerical value of the product of the concentrations of the two requisite ions $[Ca^{++}] \times [C_2O_4^{=}]$ exceeds the value of the ion-product for a saturated solution of calcium oxalate in pure water, that is, exceeds $0.0_{8}185$ (p. 479). When, on the contrary, the product of the concentrations of the two ions falls below the limiting value, a condition which may arise from the removal in some way either of the Ca^{++} or of the $C_2O_4^{=}$ ions, the undissociated molecules will ionize, and the solid will dissolve to replace them until the ionic concentrations necessary for equilibrium with the molecules have been restored or until the whole of the solid present is consumed. Here the oxalate-ion from the calcium oxalate combines with the hydrogen-ion of the acid (usually an active one) which has been added, and forms molecular oxalic acid:

$$C_2O_4^{=} + 2H^+ \leftrightarrows H_2C_2O_4. \qquad (2)$$

Hence, dissociation of the dissolved molecules of calcium oxalate proceeds, being no longer balanced by encounters and unions of the now depleted ions, and this dissociation in turn leads to solution of other molecules from the precipitate.

It will be seen that the removal of the ions in this fashion can result in considerable solution of the salt only when the acid produced is a feebly ionized one. Here, to be specific, the concentration of the $C_2O_4^{=}$ in the oxalic acid equilibrium, (2) above, must be less than that of the same ion in a saturated calcium oxalate solution. Now oxalic acid does not belong to the least active class of acids, and its pure solution contains a considerable concentration of $C_2O_4^{=}$. There is, however, a decisive factor in the situation which we have not yet taken into account. The hydrochloric acid which we used for dissolving the precipitate is a very highly ionized acid and gives an enormously greater concentration of hydrogen-ion than does oxalic acid. Hence the hydrogen-ion is in excess in equation (2), and the condition for equilibrium, $\frac{[H^+]^2 \times [C_2O_4^{=}]}{[H_2C_2O_4]} = K$, will be satisfied by a correspondingly small concentration of $C_2O_4^{=}$. In this particular case, therefore, the $[C_2O_4^{=}]$ of the oxalic acid *is* less than that given by the calcium oxalate. The whole change, therefore, depends for its accomplishment, not only on the mere presence of hydrogen-ion, but *on the repression of the ionization of the oxalic acid* by the great excess of hydrogen-ion furnished *by the active acid* that has been used. As a matter of fact, we find that a weak acid like acetic acid has scarcely any effect upon a precipitate of calcium oxalate. An acid stronger than oxalic acid must be employed. The whole scheme of the equilibria is as follows:

$$\begin{array}{lll} CaC_2O_4\text{ (solid)} \rightleftarrows & CaC_2O_4\text{ (dslvd)} & \leftrightarrows \\ & 2HCl & \leftrightarrows \end{array} \left.\begin{array}{l} Ca^{++} + C_2O_4^{=} \\ 2Cl^- + 2H^+ \end{array}\right\} \rightleftarrows H_2C_2O_4\text{ (dslvd)}.$$

When excess of an acid sufficiently active to furnish a large concentration of hydrogen-ion is employed, the last equilibrium is then driven forward and the others follow. With addition of a weak acid, only a slight displacement occurs, and the system comes to rest again when the molecular oxalic acid has reached a sufficient concentration.

A generalization may be based on these considerations: **an insoluble salt of a given acid will in general interact and dissolve when treated with a solution containing another acid, provided that the latter acid is a much more highly ionized (more active) one than the former** (see below).

But even active acids frequently fail to bring salts of weak acids into solution, especially when the weak acid is itself present also. Here the cause lies in the fact that such salts are even less soluble than those of the calcium oxalate type, and give so low a concentration of the negative ion that the utmost repression of the ionization of the corresponding acid does not give a lower value for the concentration of this ion than does the salt itself. Thus, we have seen (p. 272) that even hydrochloric acid (dilute) will not dissolve a number of sulphides. For example, in the case of cupric sulphide in a solution saturated with hydrogen sulphide, the $S^{=}$ factor in the solubility product $[Cu^{++}] \times [S^{=}]$ remains smaller than that in the scheme defining the hydrogen sulphide equilibrium $[H^{+}]^{2} \times [S^{=}]$ even when the $[S^{=}]$ factor in the latter is diminished in consequence of great addition of hydrogen-ion. In this case the first link in the chain of equilibria:

$$\left.\begin{array}{lll} \text{CuS (solid)} \leftrightarrows & \text{CuS (dslvd)} \leftrightarrows & Cu^{++} + S^{=} \\ & 2HCl & \leftrightarrows 2Cl^{-} + 2H^{+} \end{array}\right\} \rightleftarrows H_2S \text{ (dslvd)},$$

tends so decidedly backward that only the use of concentrated acid will increase the concentration of the H^{+} to an extent sufficient to secure even a slight advance of the whole action. We must add, therefore, to the above rule: **provided also that the salt is not one of extreme insolubility.** This point will be illustrated more fully in connection with the description of individual sulphides (see under Cadmium).

Illustrations of the application of these generalizations are countless. Carbonic acid is made from marble (p. 381), hydrogen sulphide from ferrous sulphide (p. 272), hydrogen peroxide from sodium peroxide (p. 222), and phosphoric acid from calcium phosphate (p. 370). In each case the acid employed to decompose the salt is more active than the acid to be liberated. On the other hand, calcium oxalate is *insoluble* in acetic acid because this acid is weaker than is oxalic acid. We have thus only to examine the list of acids showing their degrees of ionization (p. 241) in order to be able to tell which salts, if insoluble in water, will be dissolved by acids and, in general, what acids will be sufficiently active in each case for the purpose. In chemical analysis we discriminate between salts soluble in water, those soluble in acetic acid (the insoluble carbonates and some sulphides, FeS and MnS, for example), those requiring active mineral acids for their solution (calcium oxalate and the more insoluble sulphides, for example), and those insoluble in all acids (barium sulphate and other insoluble salts of active acids).

Precipitation of Insoluble Salts in Presence of Acids.— The **converse of solution,** namely, **precipitation,** depends upon the same conditions: **an insoluble salt which is dissolved by a given acid cannot be formed by precipitation in the presence of this acid.** Thus, calcium oxalate can be precipitated in presence of acetic acid, but not in presence of active mineral acids in ordinary concentrations. Cupric sulphide or barium sulphate can be precipitated in presence of any acid, but ferrous sulphide and calcium carbonate only in the absence of acids.

From this it does not follow that calcium oxalate, for example, cannot be precipitated if once an active acid has been added to the mixture. To secure precipitation, all that is necessary is to remove the excess of hydrogen-ion which is repressing the ionization of the oxalic acid. This can be done by adding a base, which removes the H^+, or even by adding sodium acetate. The acetate-ion $C_2H_3O_2^-$ unites with the H^+ to form the little ionized acetic acid, in presence of which calcium oxalate can be precipitated.

Bleaching Powder Ca(OCl)Cl.—This substance (cf. p. 309) is manufactured by conducting chlorine into a box-like structure containing slaked lime spread upon perforated shelves. When the transformation has reached the limit (it is never complete), some lime dust is blown into the chamber to absorb the remainder of the free chlorine.

That bleaching powder is a mixed salt CaCl(OCl) rather than an equimolar mixture of calcium chloride and calcium hypochlorite, which would have the same composition, $CaCl_2,Ca(OCl)_2$, is proved by the facts that the material is not deliquescent as is calcium chloride, and that calcium chloride cannot be dissolved out of it by alcohol.

Bleaching powder is somewhat soluble in water, and in solution the ions Ca^{++}, Cl^-, and ClO^- are all present. Addition of active acids causes the formation of hydrochloric and hypochlorous acids (p. 309). Weak acids like carbonic acid displace the hypochlorous acid *only* (*cf.* p. 310), and hence the dry powder, when exposed to the air, has the odor of hypochlorous anhydride Cl_2O rather than that of chlorine.

The substance is largely used by bleachers (*cf.* p. 311), and as a disinfectant to destroy germs of putrefaction and disease.

Calcium Sulphate. — This salt is found in large quantities in nature. The mineral **anhydrite** $CaSO_4$ occurs in the salt layers. It contains no water of hydration, and its crystals belong to the rhombic system. The **dihydrate,** $CaSO_4,2H_2O$, is more plentiful. In granular masses it constitutes **alabaster.** When perfectly crystallized (monoclinic system, Fig. 47, p. 83) it is named **gypsum** or **selenite.** The same hydrate is formed by precipitation from solutions. Its solubility is about 1 in 500 at 18°.

Plaster of paris $2CaSO_4,H_2O$ is manufactured by heating gypsum until nearly all the water of hydration has been driven out. When it is mixed with water, the dihydrate is quickly reformed and a rigid mass is produced. That the plaster sets rapidly, is due to the fact that the hemihydrate is more soluble than the dihydrate, and so a constant solution of the one and deposition of the other goes on until the hydration is complete. It becomes rigid, instead of forming a loose mass of dihydrate, because the process results in the formation of an interlaced and coherent mass of minute crystals.

$$2CaSO_4,H_2O\ (\text{solid}) \leftrightarrows \left.\begin{matrix}2CaSO_4\ (\text{dslvd})\\ 4H_2O\end{matrix}\right\} \leftrightarrows 2[CaSO_4,2H_2O]\ (\text{solid}).$$

Plaster of paris is used for making casts and in surgery. The setting of the material is accompanied by a slight increase in volume, and hence a very sharp reproduction of all the details of the mold is obtained. An "ivory" surface, which makes washing practicable, is conferred by painting the cast with a solution of paraffin or stearin in petroleum ether. The waxy material, left by evaporation of the volatile hydrocarbons, fills the pores and prevents solution and disintegration of the substance by water. Stucco is made with plaster of paris and rubble, and is mixed with a solution of glue instead of water.

Calcium Sulphide CaS. — This compound is most easily made by strongly heating pulverized calcium sulphate and charcoal. The sulphate is reduced: $4C + CaSO_4 \rightarrow CaS + 4CO$. Calcium sulphide is meagerly soluble in water, but is nevertheless slowly dissolved in consequence of its decomposition by hydrolysis into calcium hydroxide and calcium hydrosulphide $Ca(SH)_2$. It is used as a depilatory. Hair and wool are composed of proteins, which are decomposed by, and dissolved in alkaline solutions, like that here formed. Since calcium sulphide is thus decomposed by water it cannot be precipitated from aqueous solution by adding a soluble sulphide.

Ordinary calcium sulphide, after it has been exposed to sunlight, usually shines in the dark. Barium sulphide behaves in the same way. On this account these substances are used in making **luminous paint**. They apparently owe this behavior to the presence of traces of compounds of vanadium and bismuth, for the purified substances are not affected in the same fashion.

Phosphates of Calcium. — The **tertiary orthophosphate of calcium** $Ca_3(PO_4)_2$, known as **phosphorite**, is found in many localities, and is often derived from the remains of animals. Guano contains some of the same substance, along with nitrogen either in the form of organic compounds or as niter (p. 348). **Apatite**, $3Ca_3(PO_4)_2,CaF_2$, a double salt with calcium fluoride (or chloride), is a common mineral and frequent component of rocks. The orthophosphate forms about 83 per cent of bone ash, and is contained also in the ashes of plants. It may be precipitated by adding a soluble phosphate to a solution of a salt of calcium.

Since it is a salt of a weak acid, and belongs to the less insoluble class of such salts, calcium phosphate is dissolved by dilute mineral acids (*cf.* p. 483), the ions $HPO_4^{=}$ and $H_2PO_4^{-}$ being formed.

When a base, such as ammonium hydroxide, is added to the solution, the calcium phosphate is reprecipitated (*cf.* p. 484).

Calcium phosphate is chiefly **used** in the manufacture of phosphorus and phosphoric acid (p. 370), and as a fertilizer. The supply of calcium phosphate in the soil arises from the decomposition of rocks containing phosphates, and is gradually exhausted by the removal of crops. Bone ash is sometimes used to make up the deficiency. It is almost insoluble in water, however, and, although somewhat less insoluble in natural water containing salts like sodium chloride, is brought into a condition for absorption by the plants rather slowly. The "superphosphate" (see below) is much more soluble.

Primary calcium orthophosphate ("superphosphate") is manufactured in large quantities from phosphate rock by the action of sulphuric acid. The unconcentrated "chamber acid" is used for this purpose, as water is required in the resulting action. The amounts of material employed correspond to the equation:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 6H_2O \rightarrow Ca(H_2PO_4)_2,2H_2O + 2CaSO_4,2H_2O.$$

As soon as mixture has been effected, the action proceeds with evolution of heat, and a large cake of the two hydrated salts remains. This mixture, after being broken up, dried, and packed in bags, is sold as "superphosphate of lime." The primary phosphate which it contains is soluble in water, and is therefore of great value as a fertilizer.

Calcium Cyanamide. — Calcium carbide (p. 379), when strongly heated with nitrogen, gives a mixture of calcium cyanamide and carbon:

$$CaC_2 + N_2 \rightarrow CaCN_2 + C,$$

which is sold as **nitro-lime** for use as a fertilizer. When treated with hot water, the cyanamide is hydrolyzed into calcium carbonate and ammonia:

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3.$$

In the soil the decomposition may not be so simple, but combined nitrogen is furnished in a form that can be absorbed by plants.

At Odda (Norway) the carbide is pulverized and placed in a cylindrical furnace (Fig. 119) holding 300–450 kg. The heat (800–1000°) is supplied by the passage of an electric current through a thin carbon rod. The nitrogen is obtained by the fractionation of liquid air and final removal of all oxygen by passage over heated copper, and is forced in under pressure. After thirty-six hours, nitrogen is no longer absorbed, and the charge is pulverized when cold.

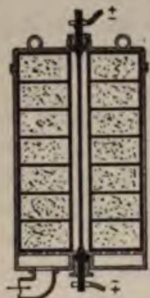

Fig. 119.

Sodium cyanide is now manufactured by fusing nitro-lime with sodium carbonate:

$$CaCN_2 + C + Na_2CO_3 \rightarrow CaCO_3 + 2NaNC.$$

The cyanide is extracted from the insoluble calcium carbonate with water, in which it is exceedingly soluble. Sodium cyanide has now displaced potassium cyanide in the extraction of gold from its ores.

Nutrition and Fertilization of Crops. — A plant constructs its cellulose, starch, and sugar, and secures the carbon-part of all its organic contents from the carbon dioxide of the air (p. 387). The water (90–95 per cent of the total weight of the plant) comes from the soil and brings up in solution the other elements required. All soils are able to supply sufficient magnesium, calcium and iron as bicarbonates. But the soil may lack: sulphur, absorbed as sulphates; nitrogen, absorbed chiefly as nitrates, but occasionally as salts of ammonium; potassium, as sulphate, chloride, or nitrate; and phosphorus, as soluble phosphates. The soil may be originally deficient in one or more of these necessary plant foods, or the supply may have been exhausted by repeated cropping. Every crop permanently removes certain quantities. For example, in the case of nitrogen, which is required to form proteins that enter largely into the fruit (*i.e.*, usually, the edible part), each crop of Indian corn (45 bushels) removes 63 pounds per acre, a crop of cabbage (15 tons) removes 100 pounds per acre, clover hay (2 tons) 82 pounds, and wheat (15 bushels) 31 pounds. When the store in the soil become meager, the crops become poor, and finally cost more for labor than they are worth.

Thus, crops have to be fed, just like cattle. Moreover, the elements must be furnished in soluble form (*cf.* pp. 137, 340, 422). Fertilizers containing potassium (p. 445, 451) and phosphorus (p. 487) must be used, when the soil is deficient in these elements. The nitrogen fertilizers we have mentioned are sodium nitrate (p. 347), calcium nitrate (p. 353), ammonium sulphate (p. 411), guano and manure (p. 348), "tankage" and ground bones from slaughter houses, calcium cyanamide (p. 487), and finally the nitrates from bacterial decomposition of root nodules (p. 339). That systematic use of fertilizers does influence the crops is indicated by the results of cultivation of land which, but for fertilization, would long since have become almost valueless. The wheat crop per acre, being the average of ten successive years is: Denmark 40 bushels, Great Britain 33, Germany 29, United States 14.

Hard Water. — As we have seen (pp. 384, 476), limestone (solubility, 0.013 g. per liter), magnesium carbonate (sol'ty 1 g. per liter), and iron carbonate, although very insoluble, are acted upon by the carbonic acid in natural waters, giving bicarbonates which are roughly about thirty times as soluble. When the water is boiled, the actions are reversed, and the carbonates are reprecipitated. These bicarbonates constitute **temporary hardness**, and their decomposition produces "fur" in a kettle and boiler crust in a boiler.

The sulphates of calcium (sol'ty 2 g. per liter) and of magnesium (sol'ty 354 g. per l) are also commonly found in natural waters. These salts are not affected by mere boiling (as distinct from evaporation) and so, along with magnesium carbonate (1 g. per l.) and calcium carbonate (0.013 g. per l.) give **permanent hardness** to the water.

Hardness is estimated in "degrees." In France, and commonly in the laboratory, 1 part of $CaCO_3$ (or its equivalent of other salts) per 100,000 (0.01 g. per liter) constitutes one degree. In the United States one degree is 1 grain per gallon of 58,333 grains (0.017 g. per l.). In Britain one degree is 1 grain per gallon of 70,000 grains (0.014 g. per l.). Well water, originating in chalk or limestone formations, may have 37° (Fr.) or more of hardness.

Damage Due to Hardness in Water. — When hard water is continually fed into a **steam boiler** and only steam comes out, naturally the salts accumulate and produce in time a heavy boiler crust, which settles on the tubes. Being a poor conductor of heat compared with iron, this crust, if one-fourth of an inch thick, will increase the consumption (and cost) of fuel by 50 per cent. In addition, the iron, not being in direct contact with water, is heated to a higher temperature, and may even become red hot. It thus oxidizes more quickly on the outside, and displaces hydrogen from water (or steam) on the inside (p. 52), thus changing on both sides gradually into the brittle magnetic oxide Fe_3O_4. If the crust is not removed, or prevented (see below), the life of the boiler is greatly shortened, and a serious explosion may even occur.

In **washing,** in the household or laundry, much soap is wasted before the necessary lather is secured. The soap, for example, the sodium stearate (p. 415), gives magnesium and calcium stearates, which are insoluble, forming a curd:

$$CaSO_4 + 2Na(CO_2C_{17}H_{35}) \rightarrow Ca(CO_2C_{17}H_{35})_2 \downarrow + Na_2SO_4.$$

The permanent solution of soap, required for washing, does not begin to be formed until all the hardness has thus been precipitated. Hence, according to the equation, with 1° (U. S.) hardness, 100 gallons (U. S.) of water should use up 0.075 pound of soap (1° Brit. and 100 gal. Brit., 0.075 lb.). In point of fact, however, the colloidal calcium salts adsorb and carry down with them more than an equal amount of undecomposed soap. Hence, actual measurement shows that, with 1° (U. S. or Brit.) of hardness, 100 gallons (U. S. or Brit.) of water really destroy 0.17 pound of soap. Thus, with 35°, no less than 6 pounds of soap per 100 gallons are wasted before the part of the soap that is to do the work begins to dissolve.

Treatment of Hard Water. — The temporary hardness can be removed by boiling the water, or using some preheating arrangement in connection with the boiler (stationary engines only).

Temporary hardness is commonly removed, on a large scale, by adding *slaked lime* (made into milk of lime) in *exactly the quantity* shown by an analysis of the water to be required, and stirring for a considerable time:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O. \qquad (1)$$

The bicarbonate is neutralized and all the lime precipitated. The latter is removed by filtration.

Permanent hardness is not affected by slaked lime, but is precipitated by adding sodium carbonate in the necessary proportion:

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4. \qquad (2)$$

When *both kinds of hardness* are present, crude caustic soda (sodium hydroxide) may be employed. It neutralizes the bicarbonate, precipitating $CaCO_3$:

$$Ca(HCO_3)_2 + 2NaOH \rightarrow CaCO_3 \downarrow + Na_2CO_3 + 2H_2O. \qquad (3)$$

and giving sodium carbonate. The latter then acts as in equation (2).

Instead of this, the treatments indicated in equations (1) and (2) may be applied in combination (Porter-Clark process).*

In the new **permutite process** the water is simply filtered through an artificial sodium silico-aluminate (permutite $Na\overline{P}$) which is supplied in the form of a coarse sand. The calcium, etc., in the water is exchanged for sodium, which does no harm:

$$Ca(HCO_3)_2 + 2Na\overline{P} \rightarrow 2NaHCO_3 + Ca\overline{P}_2.$$

After twelve hours' use, the permutite is covered with 10 per cent salt solution, and allowed to remain for the other twelve hours of the day, when it is ready for employment once more:

$$2NaCl + Ca\overline{P}_2 \rightarrow CaCl_2 + 2Na\overline{P}.$$

Only salt, which is inexpensive, is consumed, and calcium chloride solution is thrown away. Permutite removes magnesium, iron, manganese, and other elements in the same way. The life of a charge is said to be over twenty years.

Hard Water in the Laundry. — As we have seen (p. 490), soap will soften water, but the calcium and magnesium salts of the soap acids, which are precipitated, are sticky, and soil the goods being washed. Other substances that soften water not only give non-adhesive precipitates, but are also much cheaper, and an attempt is generally made to utilize them. The use of slaked lime is impracticable on a small scale.

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* So far as the hardness is due to magnesium bicarbonate, a *double* proportion of lime must be added to precipitate the magnesium as hydroxide (sol'ty 0.01 g. per l.), because the carbonate is too soluble (1 g. per l.).

Washing soda $Na_2CO_3,10H_2O$ is added to precipitate both kinds of hardness:

$$Ca(HCO_3)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaHCO_3,$$
$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4.$$

The small amounts of salts of sodium which remain in the water have no action on soap.

Household Ammonia NH_4OH acts like sodium hydroxide (p. 491):

$$Ca(HCO_3)_2 + 2NH_4OH \rightarrow CaCO_3 + (NH_4)_2CO_3 + 2H_2O,$$
$$CaSO_4 + (NH_4)_2CO_3 \rightarrow CaCO_3 + (NH_4)_2SO_4.$$

except that it will *not* precipitate magnesium-ion.

Borax $Na_2B_4O_6,10H_2O$ (p. 432) is hydrolyzed and the sodium hydroxide contained in its solution acts as already (p. 491) described.

The supposed bleaching or whitening action of borax or soda is a myth; these salts *prevent staining by the iron* in the water. They simply precipitate the iron, present as $Fe(HCO_3)_2$, which almost all waters contain, as $FeCO_3$, *before* the goods are put in. This precipitate is easily washed out in rinsing. The palmitate, etc., of iron, however, which the soap itself would throw down, is sticky and adheres to the cloth. The air subsequently oxidizes it (see p. 633) and gives hydrated ferric oxide (rust), which is brownish-red.

It is evident that, properly to achieve their purpose, the soda and borax must be added, must be completely dissolved, and must be allowed to produce the precipitation of $FeCO_3$, $CaCO_3$, etc., all *before* the soap (or the goods) is introduced. If the soap is dissolved before or with the soda, it will take part in the precipitation, and give sticky particles containing the iron and calcium salts of the soap acids.

The soda, borax, and ammonia do not themselves remove dirt — that is done by the dissolved soap (p. 418). With the help of rubbing, however, they do emulsify and remove animal or vegetable oil and grease, but not mineral oil (p. 420), when these happen to be on the goods. But soap alone will do this also, and remove mineral oil as well.

Washing powders are, or ought to be, mainly sodium carbonate, mixed with more or less pulverized soap.

Calcium Silicate $CaSiO_3$. — Calcium metasilicate $CaSiO_3$ forms the mineral wollastonite, which is rather scarce, but enters into the composition of many complex minerals, such as garnet and mica. It may be made by precipitation with a solution of sodium metasilicate (p. 428), or by fusing together powdered quartz and calcium carbonate:

$$SiO_2 + CaCO_3 \rightarrow CaSiO_3 + CO_2.$$

Glass. — Common glass is a complex silicate of sodium and calcium, or a homogeneous mixture of the silicates of these metals with silica. It has a composition represented approximately by the formula $Na_2O,CaO,6SiO_2$, and is made by melting together sodium carbonate, limestone, and pure sand:

$$Na_2CO_3 + CaCO_3 + 6SiO_2 \rightarrow Na_2O,CaO,6SiO_2 + 2CO_2.$$

For the most fusible glass, a smaller proportion of sand is employed. This variety is known, from its components, as **soda-glass,** or, from its easy fusibility, as **soft glass.** Plate-glass is made by casting the material in large sheets, rolling the sheet flat while hot, and polishing the surfaces when cold until they are plane. Window-glass is prepared by blowing bulbs of long cylindrical shape, and ripping them down one side with the help of a diamond. The resulting curved sheets are then placed on a flat surface in a furnace and are there allowed to open out. Beads are made, chiefly in Venice, by cutting narrow tubes into very short sections and rounding the sharp edges by fire. Ordinary apparatus is made of soft soda-glass, and hence when heated strongly it tends to soften and also to confer a strong yellow tint (*cf.* p. 465) on the flame. Bottles are made with impure materials, and owe their color chiefly to the silicate of iron which they contain. In all cases the articles are annealed by being passed slowly through a special furnace in which their temperature is lowered very gradually. Glass which has been suddenly chilled is in a state of tension and breaks easily when handled.

Soft glass is partially dissolved by water. When powdered glass is shaken with water, sodium silicate dissolves at once, and in amount sufficient to give an alkaline reaction with phenolphthaleïn (*cf.* p. 258).

Bohemian, or **hard glass,** is much more difficult to fuse than soda-glass, and is also much less soluble in water. It is manufactured by substituting potassium carbonate for the sodium carbonate. Specially insoluble glass, for laboratory use, such as **Jena** and **non-sol glass,** is made with boric anhydride B_2O_3, in addition to silica, and some zinc oxide, so that it contains borates as well as silicates. When lead oxide is employed instead of limestone, a soda-lead glass known as **flint glass** is produced. This has a high specific gravity, and a great refracting power for light, and is employed for making glass ornaments. By the use of grinding machinery, **cut glass** is made from it. Engraving on glass is done with the sand blast.

Colored glass is prepared by adding small amounts of various oxides to the usual materials. The oxides combine with the silica, and produce strongly colored silicates. Thus, cobalt oxide gives a blue, chromium oxide or cupric oxide a green, and uranium oxide a yellow glass. Cuprous oxide, with a reducing agent, and compounds of gold, give the free metals, suspended in colloidal solution (p. 416) in the glass, and confer a deep-red color upon it. Milk-glass contains finely powdered calcium phosphate in suspension, and white enamels are made by adding stannic oxide.

Glass is a typical amorphous substance (pp. 266, 393). From the facts that it has no crystalline structure, and that it softens gradually when warmed, instead of showing a definite melting-point, it is regarded as a supercooled liquid of extreme viscosity. Most single silicates crystallize easily, and have definite freezing- (and melting-) points. Glass may be regarded as a solution of several silicates. When kept for a considerable length of time at a temperature insufficient to render it perfectly fluid, some of its components crystallize out, the glass becomes opaque, and "devitrification" is said to have occurred. The word "crystal" popularly applied to glass is thus definitely misleading.

So-called **quartz-glass** is made of fused silica (p. 428).

Calcium-ion Ca^{++}: Analytical Reactions. — Ionic calcium is colorless. It is bivalent, and combines with negative ions. Many of the resulting salts are more or less insoluble in water. Upon the insolubility of the carbonate, phosphate, and oxalate are based tests for calcium-ion in qualitative analysis (see p. 538). The presence of the element is most easily recognized by the brick-red color its compounds confer on the Bunsen flame, and by two bands — a red and a green one — which are shown by the spectroscope.

STRONTIUM Sr

The compounds of strontium resemble closely those of calcium, both in physical properties and in chemical behavior.

Occurrence. — The carbonate of strontium $SrCO_3$ is found as **strontianite** (Strontian, a village in Argyleshire). The sulphate, **celestite** $SrSO_4$, is more plentiful. The metal may be isolated by electrolysis of the molten chloride.

Compounds of Strontium. — The compounds are all made from the natural carbonate or sulphate. The former may be dissolved directly in acids, and the latter is first reduced by means of carbon to the sulphide, and then treated with acids.

Strontium chloride $SrCl_2,6H_2O$, made in one of the above ways, is deposited from solution as the hexahydrate. The **nitrate** $Sr(NO_3)_2$ comes out of hot solutions in octahedrons which are anhydrous. From cold water the tetrahydrate $Sr(NO_3)_2,4H_2O$ is obtained. The anhydrous nitrate is mixed with sulphur, charcoal, and potassium chlorate to make "red fire." The **oxide** SrO may be secured by igniting the carbonate, but it is obtained with greater difficulty than is calcium oxide from calcium carbonate. It is generally made by heating the nitrate or hydroxide.

Strontium hydroxide $Sr(OH)_2$ is made by heating the carbonate in a current of superheated steam:

$$SrCO_3 + H_2O \rightarrow Sr(OH)_2 + CO_2.$$

This action takes place more easily than does the mere dissociation of the carbonate, because the formation of the hydroxide liberates energy, and this partially compensates for the energy which has to be provided to decompose the carbonate. The lowering of the partial pressure of the carbon dioxide by the steam also contributes to the result (*cf.* pp. 476–477). A hydrate $Sr(OH)_2,8H_2O$ crystallizes from water.

Strontium-ion Sr^{++} is bivalent, and gives insoluble compounds with carbonate-ion, sulphate-ion, and oxalate-ion. The presence of strontium is recognized by the carmine-red color which its compounds give to the Bunsen flame (see also p. 498). Its spectrum shows several red bands and a very characteristic blue line.

BARIUM Ba

The physical and chemical properties of the compounds of barium recall those of strontium and calcium. All the compounds of barium which are soluble in water, or can be brought into solution by the weak acids of the digestive fluids, are **poisonous.**

Occurrence. — Like strontium, barium is found in the form of the carbonate, **witherite** $BaCO_3$, and the sulphate $BaSO_4$, **heavy spar** or **barite** (Gk. βαρύς, heavy). The free metal, which is silver-white, may be obtained by electrolysis of the molten chloride.

The compounds are made by treating the natural carbonate with acids directly, or by first reducing the sulphate with carbon to sulphide, or converting the carbonate into oxide, and then treating the products with acids.

Compounds of Barium. — The precipitated form of **barium carbonate** $BaCO_3$ is made by adding sodium carbonate to the aqueous extract from crude barium sulphide (*q.v.*). Barium carbonate demands so high a temperature (about 1500°) for the attainment of a sufficient dissociation tension, that special means is employed for its decomposition. It is heated with powdered charcoal (*cf.* p. 385):

$$BaCO_3 + C \rightarrow BaO + 2CO.$$

Natural **barium sulphate** $BaSO_4$ is the source of many of the compounds. The precipitated sulphate, made by adding sulphuric acid to the aqueous extract from barium sulphide, is used in making white paint ("permanent white"), in filling paper for glazed cards, and sometimes as an adulterant of white lead. A mixture of barium sulphate and zinc sulphide ZnS, prepared in a special way, is called **lithopone:**

$$BaS + ZnSO_4 \rightarrow BaSO_4 \downarrow + ZnS \downarrow.$$

Made into paint it has greater covering power than white lead, does not darken with hydrogen sulphide as does the latter, and is non-poisonous. Barium sulphate is highly insoluble in water and is hardly at all affected by aqueous solutions of any chemical agents.

Barium sulphide BaS, like the sulphides of calcium and strontium (p. 273), is very slightly soluble in water, but slowly passes into solution owing to hydrolysis and formation of the hydroxide and hydrosulphide. It is made by heating the pulverized sulphate with charcoal: $BaSO_4 + 4C \rightarrow BaS + 4CO$.

Barium chloride $BaCl_2,2H_2O$ is manufactured by heating the sulphide with calcium chloride. The whole treatment of the heavy spar is carried out in one operation:

$$BaSO_4 + 4C + CaCl_2 \rightarrow 4CO + BaCl_2 + CaS.$$

By rapid extraction with water, the chloride can be separated from the calcium sulphide before much decomposition of the latter (*cf.* p. 461) has taken place.

Barium chlorate $Ba(ClO_3)_2$ is made by treating the precipitated barium carbonate with a solution of chloric acid. It is deposited in beautiful monoclinic crystals, and is used with sulphur and charcoal in the preparation of "green fire."

Barium monoxide BaO is manufactured from the carbonate (see above) or, in pure form, by heating the nitrate. The oxide unites vigorously with water to form the hydroxide.

The monoxide, when heated in a stream of air or oxygen, gives **barium peroxide**: $2BaO + O_2 \rightleftarrows 2BaO_2$, as a compact gray mass. This change and its reversal constitute the basis of Brin's process for obtaining oxygen from the air. At a suitable, high temperature, the air is forced in under pressure, causing the action to go forward, while the nitrogen escapes by a valve at the far end of the apparatus. Then, without change of temperature, by reversing the pumps, oxygen is taken out, and the reaction goes backwards. This alternation makes the process a continuous one. A **hydrate,** $BaO_2,8H_2O$, is thrown down as a crystalline precipitate when hydrogen peroxide solution is added to a solution of barium hydroxide:

$$Ba(OH)_2 + H_2O_2 \rightleftarrows BaO_2 \downarrow + 2H_2O.$$

Barium peroxide is used in the manufacture of hydrogen peroxide

Barium hydroxide $Ba(OH)_2$, is made by union of the oxide with water, or by leading moist carbon dioxide over the sulphide and decomposing the resulting carbonate with superheated steam (p. 495). It is the most soluble of the hydroxides of this group, and gives, therefore, the highest concentration of hydroxide-ion. The solution is known as "baryta-water." It is also the most stable of the three hydroxides, and may be melted without decomposition. A hydrate $Ba(OH)_2,8H_2O$ crystallizes from water.

Barium nitrate $Ba(NO_3)_2$ is made by the action of nitric acid on the sulphide, oxide, hydroxide, or carbonate of barium. The crystals from aqueous solution are anhydrous.

Analytical Reactions of the Calcium Family. — Barium-ion Ba^{++} is a colorless, bivalent ion. Many of its compounds are insoluble in water, and the sulphate is insoluble in acids also. The spectrum given by the salts contains a number of green and orange lines.

In solutions of salts of calcium, strontium, and barium, the ions may be distinguished by the fact that calcium sulphate solution will precipitate the strontium and barium as sulphates, but will leave salts of calcium in dilute solution unaffected. Similarly, strontium sulphate solution precipitates barium sulphate, and does not give any result with salts of the first two. The oxalate of calcium is precipitated in presence of acetic acid, while the oxalates of strontium and barium are not (*cf.* p. 484), and there are other differences of a like nature in the solubilities of the salts.

Exercises. — 1. Arrange the chromates of the metals of this family in the order of solubility (see Table). Compare the solubilities with those of the carbonates, oxalates, and sulphates of the metals of the same family.

2. What is meant by fluorescence (*cf.* any book on physics)?

3. What will be the ratio by volume, at 150°, of the nitrogen peroxide and oxygen given off by the decomposition of calcium nitrate? What would be the nature of the difference between the ratio at 150° and that at room temperature (*cf.* p. 352)?

4. Apply the rule of precipitation to the case of adding sodium carbonate to a solution of barium chloride.

5. Explain in terms of the ionic hypothesis the precipitation of the sulphate of strontium by calcium sulphate solution, and the absence of precipitation when the latter is added to a dilute solution of a soluble salt of calcium.

6. What inference do you draw from the fact that the oxalates of barium and strontium are not precipitated in presence of acetic acid, while the oxalate of calcium is so precipitated? Is the inference confirmed by reference to the solubility data?

7. Explain the fact that strontium and calcium chromates are easily dissolved by acetic acid, while barium chromate is dissolved only by active mineral acids.

8. Explain the fact that all the carbonates, save those of sodium, potassium, and thallium, are precipitated in neutral solutions, but not in acidified solutions. Why is the precipitation incomplete when carbon dioxide is led through solutions of salts of the metals, but more complete when the hydroxides of the metals are used?

9. Construct a table for the purpose of comparing the properties of the free elements of this family and also the properties of their corresponding compounds.

10. Are the elements of this family typical metals (p. 436)?

CHAPTER XXXVII

COPPER, SILVER, GOLD

THE three metals of this family, being found free in nature, are amongst those which were known in early times. They are the metals universally used for coinage and for ornamental purposes. They are the three best conductors of electricity (p. 436).

The Chemical Relations of the Copper Family. — **Copper** (Cu, at. wt. 63.6), **silver** (Ag, at. wt. 107.88), and **gold** (Au, at. wt. 197.2) occupy the right side in the second column of the table of the periodic system, and the chemical relations of these elements are in many ways in sharp contrast to those of the alkali metals, their neighbors, on the left side:

ALKALI METALS	COPPER, SILVER, GOLD
Very active; rapidly oxidized by air; displace all other metals from combination (E.-M. series, p. 60).	Amongst least active metals; only copper is oxidized by air; displaced by most other metals.
All univalent and give but one series of compounds. Halides all soluble in water.	Cu^{I} and Cu^{II}: two series. Ag^{I}: one series. Au^{I} and Au^{III}: two series. Chlorides of univalent series insol.
Oxides and hydroxides strongly basic, and halides not hydrolyzed (p. 437).	Oxides and hydroxides feebly basic (except Ag_2O); halides hydrolyzed (except Ag-halides). Hence, basic salts are numerous.
Never found in anion. Give no complex cations.	Frequently in anion, *e.g.*, $K.Cu(CN)_2$, $K.Ag(CN)_2$, $K.AuO_2$, $K.Au(CN)_2$, and also in complex cations, *e.g.*, $Ag(NH_3)_2.OH$ and $Cu(NH_3)_4.(OH)_2$

On account of their inactivity towards oxygen, and their easy recovery from combination by means of heat, silver and gold, together with the platinum family, are known as the "noble metals."

COPPER Cu

Chemical Relations of the Element. — Copper is the first metallic element showing two valences which we have encountered. In such cases two more or less complete, independent series of salts are known. These are here distinguished as cuprous (univalent) and cupric (bivalent) salts. The methods by which a compound of one series may be converted into the corresponding compound of the other series should be noted.

The chief cuprous compounds are Cu_2O, $CuCl$, $CuBr$, CuI, $CuCN$, Cu_2S. The cuprous compound is in each of these cases more stable (p. 93) than the corresponding cupric compound, and is formed from the latter either by spontaneous decomposition, as in the cases of the iodide and cyanide ($2CuI_2 \rightarrow 2CuI + I_2$), or on heating. The cuprous halides and cyanide are colorless and insoluble in water. Cuprous-ion Cu^+ seems to be colorless. The cuprous salts of oxygen acids have few applications.

The cupric compounds are more numerous, as they include also stable and familiar salts of oxygen acids, like $CuSO_4$, $Cu(NO_3)_2$, etc. The anhydrous salts are usually colorless or yellow, but cupric-ion Cu^{++} is blue, and so, therefore, are the aqueous solutions of the salts. The cupric are more familiar than the cuprous compounds, since cupric oxide, sulphate, and acetate are the compounds of copper which most frequently find employment in chemistry and in the arts. All the soluble salts of copper are **poisonous.**

In addition to (1) having **two valences** Cu^I and Cu^{II}, and therefore two series of compounds (*two* oxides, *two* chlorides, etc.), *each* of these states of copper also joins with other elements to form (2) **complex positive ions** such as $Cu(NH_3)_2^+$ and $Cu(NH_3)_4^{++}$, just as hydrogen and ammonia form the complex positive ion NH_4^+, and the univalent form also gives (3) stable **complex negative ions** such as $Cu(CN)_2^-$, $CuCl_2^-$. None of the metallic elements discussed in the two preceding chapters showed any of these peculiarities. Many of the metals to be discussed later exhibit one or more of them, however. **Especial attention should therefore be given to the chemistry of copper,** in order that the behavior which such relations entail may be mastered at the first encounter, and the same relations may be instantly recognized and understood when they reappear in other connections.

There is only one other peculiarity which a metallic element frequently shows, although copper does not exhibit it. This is (4) the ability of its **hydroxide** to be, not only **basic,** as metallic hydroxides by definition (p. 436) must be, **but also acidic.** This behavior we encounter first in the case of gold (see p. 520) and in simpler and more familiar form in the case of zinc (see next chapter).

Occurrence. — Copper is found free in the Lake Superior region. The sulphides, copper pyrites $CuFeS_2$ and chalcocite Cu_2S, are worked in Montana, Utah, southwest England, Spain, and Germany. Malachite, $Cu_2(OH)_2CO_3$ ($= Cu(OH)_2,CuCO_3$), a basic carbonate, is mined in Arizona, Siberia, and elsewhere. Cuprite or ruby copper Cu_2O is also an important ore.

Extraction from Ores. — For isolating native copper it is only necessary to separate the metal, by grinding and washing, from the rock through which it ramifies, and to melt the almost pure powder of copper with a flux (p. 438). The carbonate and oxide ores require coal, in addition, for the removal of the oxygen.

The liberation of copper from the sulphide ores is difficult, and often involves very elaborate schemes of treatment. This arises from the fact that many copper ores contain a large amount of the sulphides of iron, and these have to be removed by conversion into oxide (by roasting) and then into silicate (with sand). The silicate forms a flux, and separates itself from the molten mixture of copper and copper sulphide. In Montana it is found possible to abbreviate the treatment. The ore is first roasted until partially oxidized. It is then melted in a cupola or a reverberatory furnace, and placed in large iron vessels like Bessemer converters (*q.v.*) provided with a lining rich in silica. A blast of air mixed with sand is next blown through the mass. The iron is completely oxidized to FeO and made into silicate $FeSiO_3$, the sulphur escapes as sulphur dioxide, and arsenic and lead are likewise removed by this treatment. The silicate of iron floats as a slag upon the copper when the contents of the converter are poured out. The resulting copper is pure enough to be cast in large plates and purified by electrolysis (see p. 511).

Much copper ore is of low grade, containing perhaps only 2 per cent of copper ore and 98 per cent of rock material. From such ores the usual methods of washing often recover only 70 per cent or less of the copper ore present, and 30 per cent or more is lost. The **froth flotation process** raises the proportion recovered to 85 or 90 per cent of the whole. The finely crushed ore is agitated with water, to which is added some cheap oil and sometimes a little sulphuric acid. The mixture is then allowed to flow into a larger tank of water, in which the rock material immediately sinks to the bottom while the particles of ore are contained in the oily froth which rises to the top. The plant also occupies less than one-tenth of the space, and uses less than half the power required for treating the same amount of ore by washing.

The world's production (1913) is about a million metric tons, of which the United States furnished 58 per cent, South America 11, Japan 6, and Germany 4.

Physical and Chemical Properties. — Copper is red by reflected and greenish by transmitted light. It melts at 1083°, and therefore much more easily than pure iron (1530°). Sp. gr. 8.93.

In ordinary air copper becomes slowly covered with a green basic carbonate (*not* verdigris, *q.v.*). It does not decompose water at any temperature or displace hydrogen from dilute acids (p. 60). The metal attacks oxygen acids (pp. 275, 354), however. Sea-water and air slowly corrode the copper sheathings of ships, giving the basic chloride $Cu_4(OH)_6Cl_2,H_2O(=3Cu(OH)_2,CuCl_2,H_2O)$, which is found in nature as atakamite.

On account of its resistance to the action of acids, copper is used for many kinds of vessels, for covering roofs and ships' bottoms, and for coins. It furnishes also electrotype reproductions of medals, of engraved plates, of type, etc. (see p. 510). Great quantities of the metal are used in electrical plants and appliances.

Alloys. — The qualities of copper are modified for special purposes by alloying it with other metals. **Brass** contains 18–40 per cent of zinc, and melts at a lower temperature (p. 134) than does copper. A variety with little zinc is beaten into thin sheets, giving Dutch metal ("gold leaf"). **Bronze** contains 3–8 per cent of tin, 11 or more per cent of zinc, and some lead. It was used for making weapons and tools before means of hardening iron were known, and later, on account of its fusibility, continued to be employed for castings until displaced largely by cast iron (discovered in the eighteenth century). **Gun metal** contains 10 per cent, and **bell metal** 20–24 per cent of tin. **German silver** contains 19–44 per cent of zinc and 6–22 per cent of nickel, and shows none of the color of copper. In many of these alloys the metals are partly in the form of chemical compounds, such as Cu_3Sn and Cu_2Zn_3.

Cupric Chloride $CuCl_2,2H_2O$. — This compound is made by union of copper and chlorine, or by treating the hydrate or carbonate with hydrochloric acid. The blue crystals of a **hydrate,** $CuCl_2,2H_2O$, are deposited by the solution. The **anhydrous salt** is yellow. Dilute solutions are blue, the color of cupric-ion, but concentrated solutions are green on account of the presence of the yellow molecules (p. 249). The aqueous solution is acid in reaction (p. 437). When excess of ammonium hydroxide is added to the solution, the basic chloride, **cupric oxychloride** $Cu_4(OH)_6Cl_2$ (see above), which is at first precipitated, redissolves, and a deep-blue solution is obtained (see p. 506). This on evaporation yields deep-blue crystals of hydrated **ammonio-cupric chloride** $Cu(NH_3)_4.Cl_2,H_2O$. The deep-blue color of the solution, which is given by all cupric salts, is that of ammonio-cupric-ion $Cu(NH_3)_4^{++}$. The dry salt also absorbs ammonia, giving $CuCl_2,6NH_3$, but a reduction of pressure results finally in the loss of all the ammonia.

Cuprous Chloride $CuCl$. — It may be made by boiling cupric chloride solution with hydrochloric acid and copper turnings:

$$CuCl_2 + Cu \rightarrow 2CuCl, \quad \text{or} \quad Cu^{++} + Cu \rightarrow 2Cu^{+}.$$

The solution contains compounds of cuprous chloride with hydrogen chloride $HCl,CuCl$, or $HCuCl_2$ and H_2CuCl_3, which are decomposed when the acid solution is diluted with water. The cuprous chloride is insoluble in water, and forms a white crystalline precipitate.

The foregoing action is an illustration of the **fifth kind of ionic chemical change,** namely, that in which **a change in valence** (and also in the amount of the electrical charge), **occurs,** without any alteration in the composition of the ionic substance. For other illustrations see pp. 158 ($Mn^{++++} + 4Cl^{-} \rightarrow Mn^{++} + 2Cl^{-} + Cl_2$), 501.

Cuprous chloride is hydrolyzed quickly by hot water, giving, finally, red, hydrated cuprous oxide, Cu_2O. When dry it is not affected by light, but in the moist state becomes violet and, finally, nearly black. The action is said to be $2CuCl \rightarrow CuCl_2 + Cu$. In moist air it turns green, and is oxidized to cupric oxychloride (p. 504). It is dissolved by hydrochloric acid, giving the colorless complex acids $HCuCl_2$ and H_2CuCl_3 just mentioned (see below). The solution is oxidized by the air, turning first brown and then green, and finally depositing the cupric oxychloride. It also has the power of absorbing carbon monoxide, to form a compound said to be $Cu(CO)Cl,H_2O$, and the property is used to separate this gas in analyzing mixtures of gases. Cuprous chloride also dissolves (see p. 506) in ammonium hydroxide, giving **ammonio cuprous chloride** $Cu(NH_3)_2.Cl$, the ion $Cu(NH_3)_2^+$ being colorless. The solution is quickly oxidized by the air, turns deep-blue, and then contains $Cu(NH_3)_4^{++}$.

The Bromides and Iodides of Copper. — By treatment of copper with bromine-water, and slow evaporation of the solution, jet-black crystals of anhydrous **cupric bromide** $CuBr_2$ are obtained (*cf.* p. 249). When dry cupric bromide is heated, bromine is given off, and **cuprous bromide** $CuBr$ remains.

Cupric iodide CuI_2 appears to be unstable at ordinary temperatures. When a soluble iodide is added to a cupric salt, a white precipitate of **cuprous iodide** CuI and free iodine are obtained:

$$2Cu^{++} + 4I^- \leftrightarrows 2CuI\downarrow + I_2.$$

The Solution of Insoluble Salts when Complex Ions are Formed. — The solution of an insoluble salt like cuprous chloride by hydrochloric acid or ammonium hydroxide is typical of a great variety of actions of which we here meet with the first examples. Compound or complex ions are formed (*cf.* p. 501). The explanation involves only principles already used in other cases.

The dissolving of cuprous chloride in hydrochloric acid (p. 505), to form soluble, complex, highly ionized acids like $H.CuCl_2$ is a typical case. The complex negative ion $CuCl_2^-$ which is formed is very little dissociated ($CuCl_2^- \rightleftarrows Cu^+ + 2Cl^-$), and gives a smaller concentration of Cu^+ than does the insoluble cuprous chloride. The ion-product of cuprous chloride, and the concentration relations of the ionic substance $CuCl_2^-$ and its dissociation products (Cu^+ and $2Cl^-$) are symbolized as follows:

$$[Cu^+] \times [Cl^-] = K' \qquad \frac{[Cu^+] \times [Cl^-]^2}{[CuCl_2^-]} = K.$$

The value of $[\mathrm{Cu}^+]$ from cuprous chloride (first formula) is, in general, *greater* than its value from the ion $\mathrm{CuCl_2}^-$ of $\mathrm{HCuCl_2}$ (second formula), when excess of HCl is present. Hence, the Cu^+ tends to pass over into the more stable compound, where it is more completely combined. More CuCl dissolves to replace the Cu^+ which has been removed, and the change stops when the CuCl is all dissolved, or the values of $[\mathrm{Cu}^+]$ from both compounds have become equal. Thus, the complex ion is formed at the expense of the Cu^+ of the insoluble cuprous chloride, and the latter goes into solution progressively in the effort to restore the balance:

$$\left.\begin{array}{lll}\mathrm{CuCl\ (solid)} \leftrightarrows & \mathrm{CuCl\ (dslvd)} & \leftrightarrows \mathrm{Cl}^- + \mathrm{Cu}^+ \\ & \mathrm{2HCl} & \leftrightarrows 2\mathrm{H}^+ + 2\mathrm{Cl}^-\end{array}\right\} \rightleftarrows \mathrm{CuCl_2}^-\ \mathrm{(dslvd)}.$$

The same exact laws of equilibrium used in discussing the dissolving of salts by acids (p. 481) may be applied to the whole procedure.

The dissolving of cuprous chloride by the free ammonia of ammonium hydroxide is explained in the same way. The only difference is that here the copper is in a complex *positive* ion. The ion $\mathrm{Cu(NH_3)_2}^+$ gives little Cu^+ — less than does cuprous chloride, in spite of the insolubility of the latter. Hence the salt passes into solution until the ion-product $[\mathrm{Cu}^+] \times [\mathrm{Cl}^-]$, with continually increasing $[\mathrm{Cl}^-]$, reaches the value for a saturated solution or until the solid is exhausted.

The deep-colored ion $\mathrm{Cu(NH_3)_4}^{++}$ given by cupric chloride and other cupric salts is also very little ionized. Hence ammonium hydroxide dissolves all the insoluble cupric compounds save only cupric sulphide, which is the most insoluble of all — that is, the one giving the smallest concentration of cupric-ion. Conversely, the sulphide is the only insoluble compound of copper which can be precipitated from ammoniacal solution.

Foregoing Explanation Restated. — We may restate the explanation by answering a question: **Why does cuprous chloride interact with, and go into solution in hydrochloric acid?** Because **it forms a complex compound** $\mathrm{HCuCl_2}$, and, with the concentrations usually employed, **the molecular concentration of cuprous-ion in the solubility product of cuprous chloride is greater than the molecular concentration of the same ion in the solution of the complex compound.**

The answer in other cases takes the same form. Thus, for cupric hydroxide $Cu(OH)_2$ dissolving in ammonium hydroxide solution, substitute cupric hydroxide for cuprous chloride and $Cu(NH_3)_4(OH)_2$ for $HCuCl_2$.

Cuprous Oxide Cu_2O. — This oxide is red in color, and natural specimens show octahedral forms. It is produced by oxidation of finely divided copper at a gentle heat, or by the addition of bases to cuprous chloride, and is best made by the action of glucose (p. 404) on cupric hydroxide (see Fehling's solution, below). The simple **hydroxide,** CuOH, is unknown, but the above mentioned precipitate is a hydrated oxide $4Cu_2O,H_2O$, and yields Cu_2O when heated.

Cuprous oxide is acted upon by hydrochloric acid, giving cuprous chloride, or rather $HCuCl_2$. It also dissolves in ammonium hydroxide, giving, probably, $Cu(NH_3)_2.OH$, which is colorless.

Cupric Oxide and Hydroxide. — **Cupric oxide** CuO (black) is formed by heating copper in a stream of oxygen or, in less pure form, by igniting the nitrate, carbonate, or hydroxide. When heated strongly it loses some oxygen, and is partly reduced to Cu_2O.

Cupric hydroxide $Cu(OH)_2$ is precipitated as a gelatinous substance by addition of sodium or potassium hydroxide to a solution of a cupric salt: $Cu^{++} + 2OH^- \rightarrow Cu(OH)_2$. When the mixture is boiled, the hydroxide loses water and forms a black hydrated cupric oxide $Cu(OH)_2,2CuO$(?).

The hydroxide interacts with ammonium hydroxide, forming the soluble compound $Cu(NH_3)_4.(OH)_2$, which has a deep-blue color. Cellulose (cotton or paper) is soluble in this solution, and is reprecipitated by sulphuric acid. **Artificial silk** is made by pressing the solution through dies into the precipitant. Paper and cotton goods, when passed first through one and then the other of these liquids, receives a tough, **waterproof** surface.

Cupric hydroxide interacts with a solution of Rochelle salt, giving a soluble compound. The liquid is known as **Fehling's solution,** and is used in testing for, and estimating quantities of glucose (p. 404), and other reducing substances. Cuprous oxide is precipitated (see above).

Cupric Nitrate $Cu(NO_3)_2,6H_2O$. — The nitrate is made by treating cupric oxide or copper with nitric acid (p. 354), and is obtained from the solution as a deliquescent, crystalline **hexahydrate.** When dehydrated at 65° the salt is partly hydrolyzed, and a basic nitrate $Cu_4(OH)_6(NO_3)_2$ remains.

Carbonate of Copper. — No normal carbonate ($CuCO_3$) can be obtained. A **basic carbonate** (malachite) is found in nature, and is precipitated by adding soluble carbonates to cupric salts:

$$2CuSO_4 + 2Na_2CO_3 + H_2O \rightarrow Cu_2(OH)_2CO_3 + 2Na_2SO_4 + CO_2.$$

The carbonate, if formed, would be hydrolyzed by water (p. 437).

Cyanides of Copper. — With potassium cyanide and a solution of a cupric salt, **cupric cyanide** $Cu(NC)_2$ is precipitated. This is not stable, however, and gives off cyanogen, leaving **cuprous cyanide** CuNC:

$$2Cu(NC)_2 \rightarrow 2CuNC + C_2N_2.$$

Cuprous cyanide is insoluble in water, but interacts with an excess of potassium cyanide solution, producing a colorless liquid, from which $K.Cu(CN)_2$ (= KCN,CuCN), **potassium cuprocyanide,** may be obtained in colorless crystals. The complex anion $Cu(CN)_2^-$ is so little ionized to Cu^+ and $2CN^-$ that all insoluble copper compounds, *including cupric sulphide,* are dissolved by potassium cyanide; and none of them can be precipitated from the solution. Zinc is actually unable to displace copper from such a solution. The cause of the solution of the salts is the same as when the complex ions $Cu(NH_3)_2^+$, $Cu(NH_3)_4^{++}$, and $CuCl_2^-$ are formed (p. 505).

Cupric Acetate. — By the oxidation of plates of copper, separated by cloths saturated with acetic acid (vinegar), a basic acetate of copper (**verdigris**) is obtained:

$$6Cu + 8HC_2H_3O_2 + 3O_2 \rightarrow 2Cu_3(OH)_2(C_2H_3O_2)_4 + 2H_2O.$$

It is used in manufacturing green paint, is insoluble in water, and is unaffected by light. It dissolves in acetic acid, and green crystals of the **normal acetate** $Cu(C_2H_3O_2)_2,H_2O$ are obtained from the solution. The basic acetate is used in preparing **Paris green.**

Cupric Sulphate $CuSO_4$. — This salt is obtained by heating copper in a furnace with sulphur, and admitting air to oxidize the cuprous sulphide. The mixture of cupric sulphate and cupric oxide which is formed is treated with sulphuric acid. The salt is also made by allowing dilute sulphuric acid to trickle over granulated copper, while air has free access to the material:

$$2Cu + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O.$$

This is an example of the use of two reagents which separately have little or no action (*cf.* pp. 426, 431). When concentrated and very hot, sulphuric acid will itself act as the oxidizing agent (*cf.* p. 276).

Cupric sulphate crystallizes as **pentahydrate** $CuSO_4,5H_2O$ in blue asymmetric crystals (Fig. 52, p. 95), and in this form is called **bluestone** or **blue vitriol.** The aqueous solution has an acid reaction (p. 437). The anhydrous salt is white, and can be crystallized in thin needles from solution in hot, concentrated sulphuric acid (*cf.* p. 95). Cupric sulphate is employed in copper-plating (see p. 510), in batteries, and as a mordant in dyeing (*q.v.*). A minute proportion is added to drinking water, to destroy *algæ*, which otherwise propagate in the reservoirs and give a disagreeable taste and odor to the water. A solution, mixed with milk of lime ($Cu(OH)_2$ is precipitated), **Bordeaux mixture,** is largely used as a spray on grape vines and other plants to prevent the growth of fungi.

When ammonium hydroxide is added to cupric sulphate solution, a pale-green basic sulphate $Cu_4(OH)_6SO_4$(?) is first precipitated. With excess of the hydroxide, the blue $Cu(NH_3)_4^{++}$ ion (p. 506) is formed, and crystals of **ammonio-cupric sulphate** $Cu(NH_3)_4.SO_4,H_2O$ can be obtained from the solution.

Cupric sulphate also combines with potassium and ammonium sulphates, giving **double salts** of the form $CuSO_4,K_2SO_4,6H_2O$, which are deposited in large, monosymmetric crystals from the mixed solutions. Double salts (p. 245) exist as such in the solid form only and, in water, are resolved into the components and their ions.

The Sulphides of Copper. — **Cuprous sulphide** Cu_2S occurs in nature in rhombic crystals of a gray, metallic appearance. It is the sulphide formed by direct union of the elements. **Cupric sulphide** CuS is deposited as a black precipitate when hydrogen sulphide is led through a solution of a cupric salt. When heated, it leaves cuprous sulphide and sulphur vapor is given off.

Analytical Reactions of Compounds of Copper. — The ion of ordinary cupric salts, cupric-ion Cu^{++}, is blue, and that of cuprous salts, cuprous-ion Cu^{+}, is colorless. Cuprous solutions, however, are easily oxidized by the air and become blue. In solutions containing cupric-ion, hydrogen sulphide precipitates cupric sulphide, even in presence of acids (p. 483). Bases throw down the blue hydroxide, and carbonates precipitate a green basic salt (p. 508). Potassium ferrocyanide gives the brown, gelatinous **cupric ferrocyanide:**

$$2Cu.SO_4 + K_4.Fe(CN)_6 \rightleftarrows Cu_2.Fe(CN)_6 \downarrow + 2K_2SO_4.$$

A characteristic test is the formation of the deep-blue $Cu(NH_3)_4^{++}$ ion with excess of ammonium hydroxide. This solution itself responds to certain precipitants only (*e.g.*, H_2S). Solutions of complex cuprous cyanides such as $K.Cu(CN)_2$ are colorless, and do not respond to any of the above tests. With microcosmic salt or borax (pp. 371, 433), copper compounds form a bead which is blue in the oxidizing part of the flame and becomes red and opaque (liberation of copper) in the reducing flame.

Electrotyping. — When plates of platinum, connected with a battery, are immersed in cupric sulphate solution, copper is deposited on the cathode (negative pole). The sulphate-ion $SO_4^{=}$ migrates (p. 229) towards the anode (positive pole) and there liberates sulphuric acid and oxygen (p. 228). If, however, the anode is made of *copper*, the $SO_4^{=}$ migrates, but is not discharged. Instead, copper goes into solution (Fig. 120) as Cu^{++}, in amount equal to that deposited on the other pole. Thus, the only changes are, (1) an increase in concentration of cupric sulphate round the positive pole anode, and (2) a transfer of copper from the copper anode to the cathode (see, p. 511).

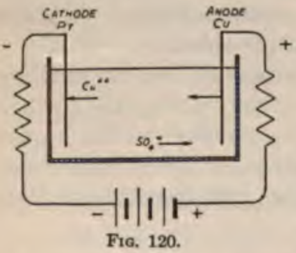

Fig. 120.

A copper **electrotype** of a medal (or a page of type) is made by first preparing a cast of the medal in plaster of Paris, gutta percha, or wax. The surface of the cast is then rubbed with graphite, to render it a conductor, and the cast is then used as the cathode in a cell with a copper anode, like that just described. The deposit of copper, when heavy enough, is stripped off. In making book plates, the cast is made with wax, and the copper electrotype is strengthened and thickened by filling the back with melted lead.*

Copper Refining. — The tenacity, ductility, and conductivity of copper are seriously affected by small amounts of impurities, such as cuprous oxide or sulphide, which are soluble in the molten metal. Arsenic amounting to 0.03 per cent lowers the conductance about 14 per cent. There are also silver and gold in smelter copper. Hence, a large proportion of the copper on the market is purified by electrolysis. The principle is the same as that used in electrotyping. Thin sheets of copper form the cathodes, and thick plates of copper the anodes. These are suspended alternately and close together in large troughs, lined with lead, and filled with cupric sulphate solution (Fig. 121, diagrammatic, view from above). The cathodes are all connected with the negative wire of the dynamo, and the anodes with the positive one. The Cu^{++} is attracted to the cathodes and is deposited upon them. The $SO_4^{=}$ migrates towards the anodes, where copper from the thick plate becomes ionized in equivalent amount. The stock of cupric sulphate thus remains the same, and the liquid is stirred to keep the sulphate from accumulating close to the anodes. The practical effect of the electrolysis is to carry copper across from one plate to the other. The cathodes are removed from time to time, and the deposit of copper is stripped from their surface. Fresh anodes are substituted when the old ones are eaten away. Since there is no final decomposi-

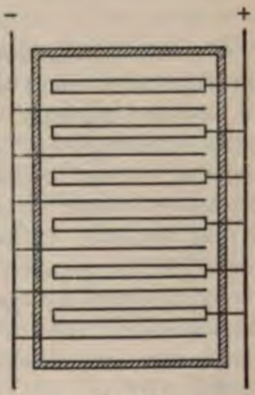

FIG. 121.

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* For newspapers, a plate is made from the cast of the type more quickly by means of melted **stereotype metal** (lead, antimony, tin; 82 : 15 : 3).

tion of any cupric sulphate, the only electrical energy required is that necessary to overcome the friction of the moving ions. Hence, a very small difference in potential (less than 0.5 volts) is sufficient (see p. 549).

The less active metals which are mixed with the copper in the anode are not ionized, because there is plenty of the more active copper to carry the current. These metals, and traces of sulphides, therefore, fall to the bottom of the vat as a sludge. Zinc and other metals more active than copper, however, *are* ionized. Conversely, at the cathode, the copper, being the least active metal present in ionic form, is alone deposited. There is no tendency to discharge zinc or hydrogen, for example, so long as there are plenty of the more easily discharged copper ions available (see. p. 549). In this way, copper, 99.8 per cent pure, is obtained, gold and silver are recovered from the sludge, and the bath liquid is removed from time to time for purification from the more active metals it acquires.

SILVER

Chemical Relations of the Element. — This element presents a curious assortment of chemical properties. It differs from copper in having a strongly basic oxide, and in giving salts with active acids which are not hydrolyzed by water. In these respects it approaches the metals of the alkalies and alkaline earths. It resembles copper in entering into complex compounds, and in giving insoluble halides. It differs from both copper and the metals of the alkalies, and resembles gold and platinum, in that its oxide is easily decomposed by heat, with formation of the free metal, and in the low position it occupies in the electromotive series and the consequent slight chemical activity of the free metal.

Occurrence. — Native silver, usually scattered through a rocky matrix, contains varying amounts of gold and copper. Native copper always contains dissolved silver. Sulphide of silver (Ag_2S) occurs alone and dissolved in galenite (PbS). Smaller amounts of the metal are obtained from pyrargyrite Ag_3SbS_3, proustite Ag_3AsS_3, and horn-silver $AgCl$. The chief supplies come from California, Australia, and Mexico.

Metallurgy.—The silver contained free, or as sulphide, in ores of copper and lead, is found in the free state dissolved in the metals extracted from these ores, and is secured by refining them. In the electrolytic refining of copper, silver is obtained from the mud deposited in the baths (p. 512). The proportion present in lead is usually small. **Parke's process,** by which the silver is separated from the lead, takes advantage of the fact that molten zinc and lead are practically insoluble in one another, while silver is much more soluble in zinc than in lead. Lead dissolves 1.6 per cent of zinc, and zinc 1.2 per cent of lead. The principle is the same as in the removal of iodine from water by ether (p. 129). The lead is melted and thoroughly mixed by machinery with a small proportion of zinc. After a short time the zinc floats to the top, carrying with it almost all of the silver, and solidifies at a temperature at which the lead is still molten. The zinc-silver alloy, largely a compound Ag_2Zn_5, is skimmed off, and heated moderately in a furnace to permit the adhering lead to drain way. The zinc is finally distilled off in clay retorts, and the lead remaining with the silver is removed by **cupellation.** This operation consists in heating the molten metal strongly in a blast of air. The lead is converted into litharge (PbO), which flows in molten condition over the edge of the cupel, and the silver is then cast.

Ores of silver which do not contain much or any lead are often smelted with lead ores, and the product is treated as described above, but many other processes are in use. The gold, which goes with the silver in Parke's process, is separated electrolytically (p. 511). Plates of the silver-gold alloy form the anode, and silver nitrate solution the vat-liquid. The silver, being the more active metal, is ionized and deposited on the cathode, while the gold collects as a powder in a bag surrounding the anode.

During the first half of the nineteenth century the world's total output of silver averaged only 643 tons per year. Up to 1870 a gram of gold could buy 15.5 g. of silver. Now that the production has reached 7800 tons, the same amount of gold purchases about 40 g. The chief sources (1911) are Mexico 2460 tons, United States 1880, Canada 1018, Europe 525.

Physical Properties.—Pure silver is almost perfectly white. It melts at 960°. Its sp. gr. is 10.5. Its ductility is such that wires can be drawn so fine that 2 kilometers weigh only about 1 g. In the molten condition it absorbs mechanically about twenty-two times its own volume of oxygen, but gives up almost all of this as it solidifies. Fantastically irregular masses result from the "sprouting" or "spitting" which accompanies the escape of the gas.

By addition of ferrous citrate to silver nitrate, a red solution and lilac precipitate of free silver can be made. The latter, after washing with ammonium nitrate solution, gives a red, colloidal solution in water (*cf.* p. 416). It is a negatively charged colloid, and is coagulated by bivalent positive ions.

Silver is alloyed with copper to render it harder. The silver coinage of the United States and the continent of Europe has a "fineness of 900" (900 parts of silver in 1000), and that of Great Britain 925. Silver ornaments have a fineness of 800 or more.

Chemical Properties. — Silver, when cold, is oxidized by ozone, but not by oxygen (see silver oxide). It does not ordinarily displace hydrogen from aqueous solutions of acids. Sulphur compounds in the air tarnish the surface, producing Ag_2S, as do also eggs, secretions from the skin (proteins, p. 422), and vulcanized rubber. Silver interacts with cold nitric acid and with hot, concentrated sulphuric acid, giving the nitrate or sulphate of silver and oxides of nitrogen or of sulphur (pp. 354, 276).

The Halides of Silver. — The **chloride** $AgCl$, **bromide** $AgBr$, and **iodide** AgI are formed as curdy precipitates when a salt of silver is added to a solution containing the appropriate halide ion. The first is white, and melts at about 457°. The second and third are very pale-yellow and yellow respectively. The insolubility in water, which is very great, increases in the above order.

When exposed to light, the chloride becomes first violet (colloidal silver, dispersed in the AgCl) and finally brown, chlorine being liberated. The bromide and iodide behave similarly. Solid silver chloride absorbs ammonia, forming at low pressures $2AgCl,3NH_3$, and with higher pressures of ammonia $AgCl,3NH_3$.

Complex Compounds of Silver. — Silver chloride dissolves easily in excess of ammonium hydroxide, giving the complex cation

$Ag(NH_3)_2^+$. The bromide, which is less readily soluble, gives the same complexion. The iodide is hardly soluble at all. Ammonio-argentic-ion $Ag(NH_3)_2^+$, in solutions of concentrations such as are commonly used (0.1*N* to *N*), gives about the same concentration of argention Ag^+ as does the bromide, and much more than the highly insoluble iodide (*cf.* p. 506). Hence the latter is almost insoluble in ammonium hydroxide, and can be precipitated in ammoniacal solution. All three of the insoluble halides interact with solutions of potassium cyanide and of sodium thiosulphate, and go into solution, as do also all the other insoluble silver salts. Usually an equivalent amount of the cyanide or thiosulphate suffices, but for complete interaction with the sulphide an excess is required. With the cyanide, double decomposition gives first the insoluble silver cyanide AgCN, which then dissolves, forming the soluble **potassium argenticyanide** $K.Ag(CN)_2$. The thiosulphate gives a solution containing the complex salt $Na_3.Ag(S_2O_3)_2$. The more active metals, like zinc and copper, displace silver from all solutions, whether the solutions contain simple or complex salts.

Oxides of Silver. — When sodium hydroxide is added to a solution of a salt of silver, a pale-brown precipitate is obtained, which, after being freed from water, is found to be **argentic oxide** Ag_2O, and not AgOH. The aqueous solution of argentic oxide, however, is distinctly alkaline, and presumably therefore does contain the hydroxide: $2AgOH \rightleftarrows Ag_2O + H_2O$. It is an active basic oxide. When moist, it absorbs carbon dioxide from the air. With ammonium hydroxide it forms the soluble $Ag(NH_3)_2.OH$. When the oxide is heated, it gives off oxygen, leaving metallic silver. The action is reversible and at 302° the dissociation pressure of the oxygen is 20.5 atmospheres. At a higher pressure than this, therefore, oxygen will combine with silver (at 302°).

Silver **peroxide** Ag_2O_2 is formed by the action of ozone on silver. In the electrolysis of silver nitrate a deposit of shining black crystals which contain some silver peroxide is formed on the anode.

Salts of Silver. — **Silver nitrate** $AgNO_3$ is obtained by treating silver with aqueous nitric acid:

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O.$$

From the solution, colorless rhombic crystals are deposited. These melt at 208.6°. Thin sticks made by casting (lunar caustic) are used to cauterize sores, because the substance combines with proteins to form insoluble compounds. The aqueous solution is *neutral.* The pure salt is not affected by light, but when deposited on cloth, on the skin of the fingers, or on the mouth of the reagent bottle, it is reduced by organic matter, and silver is liberated. For this reason it is an ingredient in some marking-inks.

Silver carbonate, the neutral salt Ag_2CO_3, and not a basic carbonate, is precipitated from solutions of salts of silver by soluble carbonates. It is slightly yellow in color. With water it gives a faint alkaline reaction and, like calcium carbonate, is soluble in excess of carbonic acid (p. 384). When heated, the carbonate decomposes, leaving metallic silver. The **sulphate** Ag_2SO_4 is made by the action of concentrated sulphuric acid on the metal. When it is mixed with a solution of aluminium sulphate (*q.v.*), octahedral crystals of **silver-alum** $Ag_2SO_4,Al_2(SO_4)_3,24H_2O$ are obtained. **Silver sulphide** Ag_2S is precipitated by hydrogen sulphide from solutions of all silver compounds, whether free acids are present or not, and irrespective of the form in which the silver is combined. *Excess* of potassium cyanide, however, prevents its precipitation from the argenticyanide. The sulphide is formed by the action of metallic silver on alkaline hydrosulphides, and this interaction forms the basis of the "hepar" test for sulphur. Silver **orthophosphate** Ag_3PO_4 (yellow), **arsenate** Ag_3AsO_4 (brown), and **chromate** Ag_2CrO_4 (crimson) are produced by precipitation, and their distinctive colors enable us to use silver nitrate in analysis as a reagent for identifying the acid radicals.

Electroplating. — The process is similar to the electrodeposition of copper (p. 510). The article to be plated is cleaned with extreme care and attached to the negative wire. A plate of silver forms the positive electrode and, since simple salts of silver do not give coherent deposits, the bath is a solution of potassium argenticyanide. The potassium-ion K^+ migrates to the negative wire and, since potassium requires a much greater E.M.F. for its liberation than does silver, silver is there deposited from the trace of argentic-ion given by the complex silver ions in the neighborhood:

$$Ag(CN)_2^- \leftrightarrows Ag^+ + 2CN^-, \quad Ag^+ + \ominus \rightarrow Ag^0.$$

At the positive electrode silver goes into solution in equivalent amount, giving argentic-ion, and the above equations are reversed.

Mirrors are silvered through the reduction of ammonio-silver nitrate by organic compounds such as formaldehyde CH_2O (formalin), or grape sugar:

$$4AgOH + CH_2O \rightarrow 3H_2O + 4Ag\downarrow + CO_2.$$

The film of silver is washed, dried, and varnished.

Photography. — Bromo-gelatine dry plates are covered with an emulsion of gelatine in which silver bromide is suspended.

After **exposure**, often for only a fraction of a second, there is no visible alteration in the film. The image is **developed.** Chemically, this consists in reducing the silver bromide to metallic silver by means of reducing agents. While the whole of the halide upon the plate is reducible, if the reducing agent is kept upon it for a sufficient length of time, the parts reached by the light are affected *first*, and with a speed proportional to the intensity of the illumination undergone by each part. The unreduced silver bromide is then dissolved out with sodium thiosulphate ("hypo"), and the silver image remains. It is also thus saved from being fogged over by the silver that would be deposited if the plate were to be brought into the light without this treatment (**fixing**). The result is a "negative," as the parts brightest in the object are now opaque, and the darkest parts of the object are transparent.

A common developer is the potassium salt of hydroquinone $C_6H_4(OH)_2$, which gives quinone $C_6H_4O_2$:

$$2AgBr + (KO)_2C_6H_4 \rightarrow 2Ag + 2KBr + C_6H_4O_2.$$

In **printing**, the light and dark are again reversed, the denser parts of the negative protecting the compounds on the paper below it from action, and leaving them white. Either "bromide" papers (such as **velox**, invented by Baekeland), which require only brief exposure and are developed like the plate, are used, or silver chloride is the sensitive substance, and prolonged exposure to light is allowed to liberate the proper amount of silver. The operation of fixing is performed as before. In **toning** chloride papers, a solution of sodium chloraurate is employed. A portion of the silver dissolves, displacing gold (p. 260), which is deposited in its place:

$$NaAuCl_4 + 3Ag \rightarrow NaCl + 3AgCl + Au.$$

The thin film of gold gives a richer color to the print.

Analytical Reactions of Silver Compounds. — Argentic-ion Ag^+ is colorless. Many of its compounds are insoluble, the precipitation of the chloride, which is insoluble in dilute acids, being used as a test. Mercurous chloride and lead chloride are also white and insoluble, but silver chloride dissolves in ammonium hydroxide, mercurous chloride (*q.v.*) turns black, and lead chloride is not altered in color (and is also soluble in hot water). With excess of ammonium hydroxide, silver salts give the complex cation $Ag(NH_3)_2^+$ and, from solutions containing silver in this form, only the iodide and sulphide can be precipitated. Sodium thiosulphate and potassium cyanide dissolve all silver salts, giving salts of complex acids with silver in the anion (p. 515).

GOLD Au

Chemical Relations of the Element. — This element forms two very incomplete series of compounds corresponding respectively to aurous and auric oxides, Au_2O and Au_2O_3. The former is a feebly basic oxide, the latter mainly acid-forming. No simple salts with oxygen acids are stable. All the compounds of gold are easily decomposed by heat with liberation of the metal. All other common metals displace gold from solutions of its compounds (p. 260). Mild reducing agents likewise liberate gold. The element enters into many complex anions.

Occurrence and Metallurgy. — Gold is found chiefly in the free condition, disseminated in veins of quartz, or mixed with alluvial sand. Small quantities are found also in sulphide ores of iron, lead, and copper. Telluride of gold (sylvanite), in which silver takes the place of a part of the gold $[Au,Ag]Te_2$, is found in Colorado.

From the alluvial deposits, gold is usually separated by washing in a cradle (sp. gr., gold 19.32, rock about 2.6), as in the Klondyke.

Quartz veins, which in the Transvaal Colony reach a thickness of a meter and carry an average of 18 g. of gold per ton, are mined, and the material is pulverized with stamping machinery. About 55 per cent of the gold is then separated by allowing the powdered rock to be carried by a stream of water over copper plates amalgamated with mercury. The gold dissolves in the latter, and is secured by removal and distillation of the amalgam. The 45 per cent of finer particles, contained in the sludge which runs off ("tailings"), are extracted by adding a dilute solution of sodium cyanide (MacArthur-Forest process) and exposing the mixture to the air. Oxidation and simultaneous interaction with the cyanide give sodium aurocyanide $NaAu(CN)_2$. From this solution the gold is isolated, either by electrolysis, or in the form of a purple powder by precipitation with zinc. The same cyanide is used for another batch.

The gold separated from ores in the above ways contains silver, copper, lead, and other metals, and various methods of refining, mainly electrolytic, are used.

The world's production of gold during the first half of the nineteenth century averaged 27 tons annually. In 1897 it was 363 tons, and in 1899, 472.6 tons. It is partly this rapid increase in the supply of gold (which is our standard of value) which has made it relatively cheaper, and other articles more expensive. In 1913 the total production was 680 tons, of which the Transvaal gave 40 per cent, the United States 20 per cent, and Australia 12 per cent.

Properties of the Metal. — Gold is yellow in color, and is the most malleable and ductile of all the metals. It melts at 1063°. Its sp. gr. is 19.32. To give it greater hardness it is alloyed with copper, the proportion of gold being defined in "carats." Pure gold is "24-carat." British sovereigns are 22-carat and contain $\frac{2}{24}$ of copper. American, French, and German coins are 21.6-carat, or 90 per cent gold.

Gold is not affected by free oxygen nor by hydrogen sulphide. It does not displace hydrogen from dilute acids, nor does it interact with nitric or sulphuric acids or any oxygen acids except selenic acid. It combines, however, with free chlorine and bromine. It interacts with a mixture of nitric and hydrochloric acids (*aqua* *regia*), giving chlorauric acid $H.AuCl_4(= HCl,AuCl_3)$. This happens, not because *aqua regia* is more active than are any of the substances it contains, but because it furnishes both the chlorine and the chloride-ion Cl^- required to produce the exceedingly stable (little dissociated) anion $AuCl_4^-$. Chlorine-water (Cl_2,H^+,Cl^-,ClO^-) dissolves it also, for the same reason. Gold is the least active of the familiar metals.

Compounds with the Halogens. — **Chlorauric acid,** formed as above, is deposited in yellow, deliquescent crystals of $H.AuCl_4,4H_2O$. The yellow sodium chloraurate $NaAuCl_4,2H_2O$, obtained by neutralization of the acid, is used in photography (p. 518). The acid gives up hydrogen chloride when heated very gently, leaving the red, crystalline **auric chloride** $AuCl_3$. When dissolved in water, this gives H_2AuCl_3O. When auric chloride is heated to 180°, **aurous chloride** $AuCl$ and chlorine are formed. This salt is a white powder. It is insoluble in water, but in boiling water is converted quickly into auric chloride and free gold: $3AuCl \rightarrow 2Au + AuCl_3 + H_2O \rightarrow H_2AuCl_3O$.

Other Compounds. — When caustic alkalies are added to chlorauric acid, or to sodium chloraurate, **auric hydroxide** $Au(OH)_3$ is precipitated. This substance is an acid, and interacts with excess of the base, forming **aurates.** These are derived from metauric acid $(Au(OH)_3 - H_2O = HAuO_2)$, as, for example, **potassium aurate** $K.AuO_2,3H_2O$. This salt interacts by double decomposition giving, for instance, with silver nitrate, the insoluble silver salt $AgAuO_2$. Its solution is alkaline in reaction, showing that auric acid is a weak acid (*cf.* p. 437). **Auric oxide** Au_2O_3 is a brown, and **aurous oxide** Au_2O is a violet powder. On account of its reducing action, hydrogen sulphide precipitates from chlorauric acid a dark-brown mixture containing much **aurous sulphide** Au_2S and free sulphur, as well as some **auric sulphide** Au_2S_3.

The **aurocyanides** like $K.Au(CN)_2(= KCN,AuCN)$, and the **auricyanides,** like $K.Au(CN)_4(= KCN,Au(CN)_3$, are formed by the action of potassium cyanide on aurous and auric compounds, respectively. They are colorless and soluble. Their solutions are used as baths, in conjunction with a gold anode, for electrogilding.

It will be seen that gold, although physically a metal, is chemically on the whole a nonmetallic element.

Assaying. — In assaying, the material containing the gold is heated with borax and lead in a small crucible (cupel) of bone ash. The lead and copper are oxidized, and their oxides are absorbed by the cupel, leaving a drop of molten alloy of gold and silver. The cold button is flattened by hammering and rolling, and treated with nitric acid to remove the silver. The gold, which remains unattacked, is washed, fused again, and weighed. The acid will not interact with the silver, and remove it completely, if the quantity of gold exceeds 25 per cent. When the proportion of gold is greater than this, a suitable amount of pure silver is fused with the alloy ("quartation").

Exercises. — 1. Write equations for the interactions, (*a*) of salt water and oxygen with copper (p. 503), (*b*) of ferrous oxide and sand (p. 502).

2. Write the formulæ of the basic chloride, nitrate, carbonate, and sulphate of copper as if these substances were composed of the normal salt, the oxide and water (p. 369).

3. Can you develop any relation between the facts that solutions of cupric salts are acid in reaction and that they give basic carbonates by precipitation?

4. Formulate the action of potassium cyanide in dissolving cupric hydroxide and cuprous sulphide, assuming that potassium cuprocyanide is formed.

5. How should you set about making cupric orthophosphate, ammonium cuprocyanide, and lead cuprocyanide?

6. Write the formulæ of some of the double salts analogous to potassium-cupric sulphate (p. 509).

7. What chemical reagents are present in a Bunsen flame? If borax beads were made in the oxidizing flame with cupric chloride, cuprous bromide, and cupric sulphate, severally, what actions would take place?

8. Write the equations for the interaction of, (*a*) silver and concentrated sulphuric acid, (*b*) silver chloride and sodium carbonate when heated strongly, (*c*) sodium thiosulphate and silver bromide.

9. What reagents should you use to precipitate the phosphate, arsenate, and chromate of silver?

10. Write the equations for the interactions of, (*a*) potassium hydroxide and auric hydroxide, (*b*) potassium cyanide and sodium chloraurate.

11. In what respects are the elements of this family distinctly metallic, and in what respects are they allied to the non-metals (p. 436)?

12. Collect all the evidence tending to show that the cuprous compounds are more stable than the cupric.

13. Make a classified list of the methods by which cupric compounds are transformed into cuprous, and *vice versa*.

14. Of which metals should it be possible to obtain colloidal suspensions in water, and of which not (p. 260)? Suggest some liquids in which you should expect to obtain colloidal suspensions of the alkali metals.

CHAPTER XXXVIII

GLUCINUM, MAGNESIUM, ZINC, CADMIUM, MERCURY. THE RECOGNITION OF CATIONS IN QUALITATIVE ANALYSIS

The Chemical Relations of the Family. — The remaining elements of the third column of the periodic table, namely **glucinum** or **beryllium** (Gl, or Be, at. wt. 9.1), **magnesium** (Mg, at. wt. 24.32), **zinc** (Zn, at. wt. 65.4), **cadmium** (Cd, at wt. 112.4), and **mercury** (Hg, at. wt. 200.6), although all bivalent, do not form a coherent family. Glucinum and magnesium resemble zinc and cadmium, and differ from the calcium family, in that the sulphates are soluble, the hydroxides easily lose water leaving the oxides, and the metals are not rapidly rusted in the air and do not easily displace hydrogen from water. They resemble the calcium family, and differ from zinc and cadmium, in that the sulphides are hydrolyzed by water, the oxides are not reduced by heating with carbon, complex cations are not formed with ammonia, and the metals do not enter into complex anions. But glucinum differs from magnesium and resembles zinc in that its hydroxide is acidic as well as basic. This is not unnatural, since in the periodic system it lies between lithium, a metal, and boron, a non-metal. Mercury is the only member of the group that forms two series of compounds. These are derived from the oxides HgO and Hg_2O. Mercury approaches the noble metals in the ease with which its oxide is decomposed by heating, and in the position of the free element in the electromotive series.

The vapor densities of zinc, cadmium, and mercury show the vapors of these three metals to be monatomic.

GLUCINUM Gl

Glucinum (or beryllium) is bivalent in all its compounds. Its oxide and hydroxide are basic, and are also feebly acidic towards active bases (see Zinc hydroxide). The element derives its name from the sweet taste of its salts (Gk. γλυκύς, sweet).

Glucinum occurs in beryl, a metasilicate of glucinum and aluminium $Gl_3Al_2(SiO_3)_6$. Beryls, tinted green by the presence of a little silicate of chromium, are known as **emeralds**. The metal, obtained by electrolysis of the easily fusible double fluoride $GlF_2,2KF$, burns when heated in the air. It displaces hydrogen from dilute acids, and when heated, from caustic potash: $Gl+2KOH \rightarrow K_2GlO_2+H_2$.

MAGNESIUM Mg

Chemical Relations of the Element. — Magnesium is bivalent in all its compounds. The oxide and hydroxide are basic exclusively. The element does not enter into complex cations or anions.

Occurrence. — Magnesium carbonate occurs alone as magnesite, and in a double salt with calcium carbonate $MgCO_3,CaCO_3$ as dolomite. The sulphate and chloride are found as hydrates and as constituents of double salts (see below) in the Stassfurt deposits. Olivine is the orthosilicate Mg_2SiO_4. Talc (soapstone) is an acid metasilicate $H_2Mg_3(SiO_3)_4$. Serpentine is a hydrated disilicate, $[Mg,Fe]_3,Si_2O_7,2H_2O$, as is also meerschaum. Asbestos is an anhydrous silicate. The element derives its name from Magnesia, a town in Asia Minor.

The Metal. — Magnesium is manufactured by electrolysis of dehydrated and fused carnallite $MgCl_2,KCl,6H_2O$. The iron crucible in which the material is melted forms the cathode, and a rod of carbon the anode. The metal is silver-white, and when heated can be pressed into wire and rolled into ribbon (m.-p. 651°).

Chemically the metal is less active than are the metals of the alkaline earths. It slowly becomes coated with a layer of the carbonate. It displaces hydrogen slowly from boiling water and rapidly from cold, dilute acids. Magnesium burns in air with a white light. The ash contains the **nitride** Mg_3N_2, as well as the oxide.

Powdered magnesium is used in pyrotechny and, with potassium chlorate (10 : 17), in making flashlight powder for use in photography.

Magnesium Chloride $MgCl_2,6H_2O$. — This highly deliquescent salt occurs in salt deposits, alone, and as carnallite $MgCl_2$,-

$KCl,6H_2O$. The latter is an important source of potassium chloride (p. 445), and almost all the magnesium chloride combined with it is thrown away. When the hexahydrate is heated, a part of the chloride is hydrolyzed, some magnesium oxide remaining, and some hydrogen chloride being given off. Sea-water cannot be used in ships' boilers because of the hydrochloric acid thus liberated by the action of the magnesium chloride which the water contains. **Anhydrous** magnesium chloride $MgCl_2$ is obtained by heating the double chloride $MgCl_2,NH_4Cl,6H_2O$, for this salt can be dehydrated without hydrolysis of the chloride. The ammonium chloride is volatilized (p. 453).

The Oxide and Hydroxide. — **Magnesium oxide** MgO is made by heating the carbonate, and is known as **calcined magnesia.** It is a white, highly infusible powder, and is used for lining electric furnaces and making crucibles. It combines slowly with water to form the hydroxide $Mg(OH)_2$.

The **hydroxide** is found in nature as brucite. It is also precipitated from solutions of magnesium salts by alkalies. It is very slightly soluble in water. The solution has a faint alkaline reaction. When magnesium chloride is added to the moist hydroxide, a hydrated basic chloride, $(Mg(OH)_2)_x,(MgCl_2)_y,(H_2O)_z$, is formed. The mixture, to which sawdust is sometimes added, is used as a plaster-finish in building.

Magnesium hydroxide is not precipitated by ammonium hydroxide when ammonium salts are present also. The ammonium salts, being highly ionized and giving a high concentration of ammonium-ion NH_4^+, repress the ionization of the feebly ionized ammonium hydroxide, and so reduce the concentration of hydroxide-ion which it furnishes. With the ordinary concentration of Mg^{++}, therefore, the amount of hydroxide-ion existing in presence of excess of a salt of ammonium is too small to bring the solubility product $[Mg^{++}] \times [OH^-]^2$ up to the value required for precipitation (*cf.* p. 479). Conversely, magnesium hydroxide interacts with solutions of ammonium salts and passes into solution:

$$\begin{array}{rcl}\mathrm{Mg(OH)_2(solid)} \rightleftarrows & \mathrm{Mg(OH)_2\ (dslvd)} & \rightleftarrows \mathrm{Mg^{++} + 2OH^-} \\ & \mathrm{2NH_4Cl} & \rightleftarrows \mathrm{2Cl^- + 2NH_4^+}\end{array}\left.\vphantom{\begin{array}{c}a\\b\end{array}}\right\}\rightleftarrows \mathrm{2NH_4OH}.$$

In presence of excess of ammonium chloride, the OH^- combines with NH_4^+ to form molecular ammonium hydroxide, and the equilibria in the upper line are displaced forwards to generate a further supply of the OH^-. With sufficiently great concentration of the ammonium chloride, all the magnesium hydroxide may thus dissolve. The whole case is analogous to the interaction of acids with insoluble salts (p. 480).

Other Salts of Magnesium. — The normal **carbonate** $MgCO_3$ is found in nature. Only hydrated *basic* carbonates are formed by precipitation, and their composition varies with the conditions. The carbonate, manufactured in large amounts and sold as **magnesia alba,** is approximately $Mg_4(OH)_2(CO_3)_3.3H_2O$. It is used in medicine and as a cosmetic.

The common **heptahydrate** of **magnesium sulphate** $MgSO_4,7H_2O$ crystallizes from cold water in rhombic prisms, and is called **Epsom salts.** It is efflorescent. The **monohydrate** $MgSO_4,H_2O$, which remains, and is found also in the salt layers as kieserite, has a very low aqueous tension, and is not rapidly dehydrated except above 200°. Magnesium sulphate is used in the manufacture of sodium and potassium sulphates, and is employed also for "loading" cotton goods, and as a purgative.

The **sulphide** MgS may be formed by heating the metal with sulphur. It is insoluble in water, but is decomposed and gives, finally, hydrogen sulphide and magnesium hydroxide:

$$MgS + 2H_2O \rightleftarrows Mg(OH)_2\downarrow + H_2S.$$

The only **phosphate** of importance is ammonium-magnesium orthophosphate $NH_4MgPO_4,6H_2O$, which appears as a crystalline precipitate when sodium phosphate and ammonium hydroxide (and chloride, p. 525) are mixed with a solution of a magnesium salt.

Analytical Reactions of Magnesium Compounds. — The magnesium ion is colorless and bivalent. Soluble carbonates precipitate basic carbonates of magnesium, but not when ammonium salts are present. The latter limitation distinguishes compounds of magnesium from those of the calcium family. Sodium hydroxide precipitates the hydroxide of magnesium, except when salts of ammonium are present. The mixed phosphate of ammonium and magnesium, in presence of ammonium hydroxide, is the least soluble salt.

ZINC Zn

Chemical Relations of the Element. — Zinc is bivalent in all its compounds. Of these there are two sets, — the more numerous and important one, in which zinc is the positive radical ($Zn.SO_4$, $Zn.Cl_2$, etc.), and a less numerous set, the zincates, in which zinc is in the negative radical ($Na_2.ZnO_2$, etc.). Both sets of salts are hydrolyzed by water, as the hydroxide is feeble whether it is considered as an acid or as a base. The element also enters into complex cations and anions. The salts are all **poisonous.**

Occurrence and Extraction from the Ores. — The chief sources of zinc are calamine Zn_2SiO_4,H_2O, smithsonite $ZnCO_3$, zinc-blende (Ger. *blenden*, to dazzle) or sphalerite ZnS, franklinite $Zn(FeO_2)_2$, and zincite ZnO.

The ores are first concentrated, recently by froth flotation (p. 503). They are then converted into oxide — the carbonate by ignition, and the sulphide by roasting. The sulphur dioxide is used to make sulphuric acid. A mixture of the oxide with coal is then distilled in earthenware retorts at 1300–1400°; the zinc condensing in earthenware receivers, while carbon monoxide burns at a small opening:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2,$$
$$ZnO + C \rightarrow CO + Zn.$$

At first zinc dust (a mixture of zinc and zinc oxide) collects in the receiver, and afterwards liquid zinc. The product, which is cast in blocks, is called spelter.

Properties and Uses of the Metal. — Zinc is a bluish-white crystalline metal. When cold it is brittle, but at 120–150° it can be rolled into sheets between heated rollers and then retains its pliability when cold. At 200–300° the metal becomes once more brittle, at 419° it melts, and at 925° it boils. The vapor at 1740° is monatomic.

The metal burns in air with a greenish flame, giving zinc oxide. In cold, moist air it is very slowly oxidized, and becomes covered with a firmly adhering, non-porous layer of basic carbonate which protects it from further action. The metal displaces hydrogen from dilute acids. Zinc also attacks boiling alkalies, giving the soluble zincate (see below): $2KOH + Zn \rightarrow K_2ZnO_2 + H_2$.

Sheet zinc, in consequence of its lightness (sp. gr. 7), is **used** in preference to lead (sp. gr. 11.5) for roofs, gutters, and architectural ornaments. Galvanized iron is made by dipping sheet iron, cleaned with sulphuric acid or the sand blast, into molten zinc. The latter, being more active (p. 260), is rusted instead of the iron, but the rusting is very slight (see above). Objects of iron, cleaned and baked in zinc dust, also acquire a coating of zinc (sherardizing). Zinc is used also in batteries and for making alloys (p. 435). It mixes in all proportions with tin, copper, and antimony.

Zinc Chloride $ZnCl_2$. — This salt is usually manufactured by treating zinc with *excess* of hydrochloric acid, evaporating the solution to dryness, and fusing the residue. When hydrochloric acid is thus present, the chloride $ZnCl_2$ is obtained. Evaporation of the pure aqueous solution, which is acid in reaction, results in considerable hydrolysis and formation of much of the basic chloride Zn_2OCl_2:

$$ZnCl_2 + H_2O \rightleftarrows HCl + Zn(OH)Cl, \quad (1)$$

$$2Zn(OH)Cl \rightarrow Zn_2OCl_2 + H_2O. \quad (2)$$

The salt is **used** in solid form as a caustic and, by injection of a solution into wood (*e.g.*, railway sleepers), as a poison to prevent the growth of organisms which promote decay. In both cases the salt combines with proteins, forming solid products. The hot solution also dissolves cellulose (cotton or paper). When the solution is pressed through an orifice into alcohol, the cellulose is precipitated in the form of a thread. By carbonizing such threads, carbon filaments for incandescent lamps are made.

Zinc Oxide and Hydroxide and the Zincates. — The **oxide** ZnO is obtained as a white powder by burning zinc or by heating the precipitated basic carbonate. It turns yellow when heated, recovering its whiteness when cold, in the same way that mercuric oxide is brown whilst hot and bright red when cold. It is **employed** in making a paint — zinc-white or Chinese white — which is not darkened by hydrogen sulphide. It is used also as a filler in making rubber automobile tires.

The **hydroxide** $Zn(OH)_2$ appears as a white, flocculent solid when alkalies are added to solutions of zinc salts. It interacts as a basic hydroxide with acids, giving salts of zinc:

$$Zn(OH)_2 + H_2SO_4 \leftrightarrows Zn.SO_4 + 2H_2O.$$

It also interacts with excess of the alkali employed to precipitate it, giving a soluble **zincate**, such as **potassium zincate** K_2ZnO_2:

$$H_2ZnO_2\uparrow + 2KOH \rightleftarrows K_2.ZnO_2 + 2H_2O.$$

Zinc hydroxide is ionized both as an acid and as a base:

$$\begin{array}{rcl} 2H^+ + ZnO_2^{=} \rightleftarrows & Zn(OH)_2 \text{ (dslvd)} & \rightleftarrows Zn^{++} + 2OH^- \\ & \downarrow\uparrow & \\ & Zn(OH_2) \text{ (solid)} & \end{array}$$

Substances which are both bases and acids are called **amphoteric.** The ionization as an acid is less than that as a base, but both are small. Addition of an acid like sulphuric acid, however, furnishes hydrogen-ion; the hydroxyl ions combine with this to form water, and all the equilibria are displaced to the right. With a base, on the other hand, the hydrogen-ion is removed and the basic ionization simultaneously repressed, so that the equilibria are displaced to the left.

Zinc hydroxide interacts with ammonium hydroxide, giving the soluble **ammonio-zinc hydroxide** $Zn(NH_3)_4.(OH)_2$. The case is like those of copper (p. 507) and silver hydroxides (p. 515).

Compounds of zinc, when heated in the Bunsen flame with a salt of cobalt, give a **zincate of cobalt** (Rinmann's green) $CoZnO_2$.

Other Salts of Zinc. — The normal **zinc carbonate** $ZnCO_3$ may be precipitated by means of sodium bicarbonate, but normal carbonate of sodium gives **basic carbonates,** such as $Zn_2(OH)_2CO_3$:

$$2ZnSO_4 + 2Na_2CO_3 + H_2O \rightarrow Zn_2(OH)_2CO_3 + 2Na_2SO_4 + CO_2\uparrow.$$

Zinc sulphate $ZnSO_4$ is formed when zinc-blende is roasted. It gives rhombic crystals of the **hydrate** $ZnSO_4,7H_2O$. This, and the corresponding compounds of magnesium $MgSO_4,7H_2O$, of iron $FeSO_4,7H_2O$, and of other bivalent metals are known as **vitriols.** The zinc salt is **white vitriol.** It is **used** in cotton-printing and as an eye-wash ($\frac{1}{8}$ per cent solution). The sulphate gives double salts, such as **potassium-zinc sulphate** $ZnSO_4,K_2SO_4,6H_2O$ (*cf.* p. 509).

Zinc sulphide ZnS is more soluble in water than is sulphide of copper, and hence it interacts with excess of strong acids, and passes into solution. It is not soluble enough, however, to be much affected by weak acids like acetic acid (*cf.* p. 483). Zinc sulphide is thus capable of being precipitated when acetic acid is present, or when hydrogen sulphide is led into a solution of the acetate of zinc:

$$Zn(C_2H_3O_2)_2 + H_2S \rightleftarrows ZnS\downarrow + 2HC_2H_3O_2.$$

But when an active acid is present, or is formed, the sulphide is precipitated incompletely or not at all, the action being reversible:

$$ZnSO_4 + H_2S \rightleftarrows ZnS + H_2SO_4.$$

There are thus two ways of obtaining the sulphide by precipitation. A soluble sulphide causes it to be thrown down completely, because no acid is liberated in the action:

$$ZnCl_2 + (NH_4)_2S \rightleftarrows ZnS\downarrow + 2NH_4Cl.$$

The other method is to add sodium acetate to the solution of the salt, and then lead in hydrogen sulphide. The acid, liberated by the action upon the salt, interacts with the sodium acetate, giving a neutral salt of sodium and acetic acid, and the zinc sulphide is not much affected by the latter (*cf.* p. 484). For **uses,** see lithopone (p. 497).

Analytical Reactions of Zinc Salts. — Zinc sulphide is precipitated by the addition of ammonium sulphide to solutions of zinc salts and of zincates. Sodium hydroxide gives the insoluble hydroxide, which, however, interacts with excess of the alkali, giving the soluble zincate of sodium. Compounds of zinc, when heated on charcoal with cobalt nitrate, give Rinmann's green (p. 529).

CADMIUM Cd

Chemical Relations of the Element. — This element is bivalent in all its compounds. Its oxide and hydroxide are basic exclusively, and the salts are not hydrolyzed by water. It enters into complex compounds having the ions $Cd(NH_3)_4^{++}$ and $Cd(CN)_4^{=}$. Note its resemblances to, and differences from zinc.

The Metal. — Aside from the rare mineral greenockite CdS, cadmium is found in small amounts (about 0.5 per cent), as carbonate and sulphide, in the corresponding ores of zinc. During the reduction, being more volatile than zinc, it distils over first (b.-p. 778°). The metal is white, and is more malleable than zinc.

It displaces hydrogen from dilute acids (*cf.* p. 260). It is **used** in making fusible alloys.

Compounds of Cadmium.—The **chloride** $CdCl_2,2H_2O$ is efflorescent and is not hydrolyzed during dehydration or in solution. Zinc chloride (p. 528) is deliquescent and is easily hydrolyzed.

The **hydroxide** $Cd(OH)_2$ is made by precipitation (white), and interacts with acids (as a basic hydroxide), but not at all with bases. It dissolves in ammonium hydroxide, however, forming $Cd(NH_3)_4.(OH)_2$. The **oxide** CdO is a brown powder, obtained by heating the hydroxide, carbonate, or nitrate, or by burning the metal.

The **sulphate** crystallizes from solution as $3CdSO_4,8H_2O$. Soluble carbonates throw down the **normal carbonate** of cadmium $CdCO_3$.

Hydrogen sulphide precipitates the yellow **sulphide** CdS even from acid solutions of the salts. The substance is used as a pigment. The sulphide of cadmium, however, is less insoluble in water (*cf.* p. 483) than are the sulphides of copper and mercury, and is not completely precipitated from a strongly acid solution (*e.g.*, $HCl > 0.3N$).

The Solubilities of the Sulphides of the Metals.—The reader will remember the order of solubility of the metallic sulphides more easily if he notes that it is practically the same as the order of activity of the free metals (p. 260 or Appendix V). Thus, the sulphides down to that of aluminium are dissolved by water (K_2S and Na_2S) or are decomposed by water (BaS, SrS, CaS, MgS, Al_2S_3). The hydroxides formed, being soluble (except $Al(OH_3)$), the whole dissolves except in the case of Al_2S_3. Zinc sulphide is insoluble in water, but is soluble enough to interact with (and dissolve in) dilute acids, even a feeble one like acetic acid. Ferrous sulphide requires a dilute *active* acid; cadmium sulphide requires a higher concentration of an active acid, as do also CoS and NiS; cupric sulphide requires an oxidizing acid like hot nitric acid; and mercuric sulphide resists even this.

Analytical Reactions of Cadmium Compounds.—The cadmium ion Cd^{++} is bivalent and colorless. The yellow cadmium sulphide is precipitated by hydrogen sulphide, even from acid solutions of the salts. The white, insoluble hydroxide is not soluble in sodium hydroxide.

MERCURY Hg

Chemical Relations of the Element. — Like copper, this element enters into **two series of** compounds, the **mercurous** Hg^{I} and the **mercuric** Hg^{II}. The mercurous halides, like the cuprous halides (and the argentic halides), are insoluble in water and are decomposed by light. Both of the oxides, Hg_2O and HgO, are basic exclusively, but in a feeble degree. The hydroxides, like silver hydroxide, are not stable, and lose water, giving the oxides. The salts of both sets are markedly hydrolyzed by water, and basic salts are therefore common. No carbonate is known. Mercury enters into the anions of a number of complex salts, such as $HgCl_4^{=}$, $HgI_4^{=}$, $Hg(CN)_4^{=}$, etc. It forms a class of ammono-basic mercury compounds, like $Hg^{II}NH_2Cl$, all of which are insoluble.

The mercury salts of volatile acids, like the corresponding salts of ammonium (p. 345), can all be volatilized completely. Mercury vapor and all mercury compounds are **poisonous,** the soluble ones more markedly so than the insoluble ones.

Occurrence and Isolation of the Metal. — Mercury occurs native and to a larger extent as red, crystalline cinnabar, mercuric sulphide HgS. The chief mines are in Spain, Italy, Austria, and California.

The liberation of the metal is easy, because, when roasted, the sulphide is decomposed, and the sulphur forms sulphur dioxide. The mercury does not unite with the oxygen, for the oxide decomposes (p. 14) at 400–600°:

$$HgS + O_2 \rightarrow Hg + SO_2.$$

In some places the ore is spread on perforated brick shelves in a vertical furnace, and the gases pass through tortuous flues in which the vapor of the metal condenses.

Physical Properties. — Mercury or quicksilver (N.L. *hydrargyrum,* from Gk. ὕδωρ, water, and ἄργυρος, silver) is a silver-white liquid. At − 38.7° it freezes, and at 357° it boils.

On account of its high specific gravity (13.6, at 0°) and low vapor tension, the metal is employed for filling barometers. Its uniform expansion favors its use in thermometers. It forms amalgams with all the familiar metals, with the exception of iron and platinum. The latter, however, is "wet" by it (*cf.* pp. 345, 519). Compounds, such as $NaHg_2$, are often present in amalgams.

Chemical Properties. — When kept at a temperature near to its boiling-point, mercury combines slowly with oxygen. Mercury does not displace hydrogen from dilute acids (p. 260), but with oxidizing acids like nitric acid and hot concentrated sulphuric acid, the nitrates and sulphate (mercuric) are formed. With excess of mercury, mercurous nitrate, and with excess of the hot acid, mercuric nitrate, are produced. When mercury is divided into minute droplets, with relatively large surface, it is used in medicine ("blue pills"), and shows an activity which is entirely wanting in larger masses.

The Halides of Mercury. — **Mercurous chloride** $HgCl$ (**calomel**) is obtained as a white powder by precipitation. It is made by subliming mercuric chloride with mercury:

$$HgCl_2 + Hg \rightleftarrows 2HgCl,$$

or more usually by subliming a mixture of mercuric sulphate, made as described above, with mercury and common salt. It is deposited on the cool part of the vessel as a fibrous crystalline mass. Its vapor is composed entirely of mercury and mercuric chloride. It is slowly affected by light just as is silver chloride. Here, however, the chlorine which is released combines with another molecule of the salt to form mercuric chloride. The substance is **used** in medicine on account of its tendency to stimulate all organs producing secretions.

By direct union with chlorine, **mercuric chloride** $HgCl_2$ (**corrosive sublimate**) is formed. It is usually manufactured by subliming mercuric sulphate with common salt, and crystallizes in white, rhombic prisms. It melts at 265° and boils at 307°. The solubility at 20° is 7.4 : 100 Aq. The aqueous solution is slightly acid in reaction. The salt is easily reduced to mercurous chloride. When excess of stannous chloride is added to the solution, the white precipitate of calomel, first formed, passes into a heavy gray precipitate of finely divided mercury:

$$2HgCl_2 + SnCl_2 \rightarrow SnCl_4 + 2HgCl,$$
$$2HgCl + SnCl_2 \rightarrow SnCl_4 + 2Hg.$$

Corrosive sublimate, when taken internally, is extremely poisonous. A very dilute solution (1 : 1000) is used in surgery to destroy lower organisms and thus prevent infection of wounds. Mercuric chloride acts also as a preservative of zoölogical materials, forming insoluble compounds with proteins, and preventing decay. For the same reason, albumin (white of an egg) is given as an antidote in cases of sublimate poisoning.

Mercurous iodide HgI is formed by rubbing iodine with excess of mercury. It also appears as a greenish-yellow precipitate when potassium iodide is added to a solution of a mercurous salt. It decomposes spontaneously into mercury and mercuric iodide:

$$2HgI \rightleftarrows Hg + HgI_2.$$

Mercuric iodide HgI_2 is obtained by direct union of mercury with excess of iodine, or by addition of potassium iodide to a solution of a mercuric salt. It is a scarlet powder, insoluble in water, but soluble in alcohol and ether. It interacts with excess of potassium iodide, forming the soluble, colorless **potassium mercuri-iodide** $K_2.HgI_4$ with which many precipitants fail to give mercury compounds.

The Oxides. — When bases (excepting ammonium hydroxide, see p. 535) are added to solutions of mercurous salts, the greenish-black **mercurous oxide** Hg_2O is thrown down. The hydroxide is doubtless formed transitorily and then loses water (*cf.* Silver oxide, p. 515). Under the influence of light or gentle heat (100°), this oxide resolves itself into mercuric oxide and mercury.

Mercuric oxide HgO is formed as a red, crystalline powder, when mercury is heated in air near to 357°, but is usually made by decomposing the nitrate. Commercial specimens, incompletely decomposed, thus give some nitrogen tetroxide when heated. It is formed also as a yellow powder by adding bases (excepting ammonium hydroxide, see p. 535) to solutions of mercuric salts.

Other Salts of Mercury. — **Mercurous nitrate** $HgNO_3,H_2O$ is formed by the action of cold, diluted nitric acid upon *excess* of mercury. It is hydrolyzed, slowly by cold, and rapidly by warm water, giving an insoluble basic nitrate:

$$2HgNO_3 + H_2O \rightleftarrows HNO_3 + Hg_2(OH)NO_3\downarrow.$$

On this account a clear solution can be made only when some nitric acid is added. Free mercury is also kept in the solution to reduce mercuric nitrate, which is formed by atmospheric oxidation:

$$Hg(NO_3)_2 + Hg \rightarrow 2HgNO_3, \quad \text{or} \quad Hg^{++} + Hg \rightarrow 2Hg^{+}.$$

Mercuric nitrate $Hg(NO_3)_2,8H_2O$ is produced by using excess of warm, concentrated nitric acid with mercury. The aqueous solution is strongly acid, and deposits a yellowish, crystalline, basic nitrate $Hg_3(OH)_2O(NO_3)_2$. The hydrolysis is reversed by adding nitric acid.

Mercurous sulphide Hg_2S is formed by precipitation from mercurous salts, but decomposes into mercury and mercuric sulphide.

Crystallized **mercuric sulphide** HgS occurs as cinnabar, and is red. When formed by precipitation with hydrogen sulphide, or by rubbing together mercury and sulphur, it is black and amorphous. By sublimation, in the course of which it dissociates and recombines, the black form gives the red, crystalline one.

The black and the red varieties do not interact with concentrated acids, or even with boiling nitric acid, which oxidizes most sulphides readily. They are, therefore, still less soluble than is cupric sulphide (pp. 483, 531). They are attacked, however, by *aqua regia*, because of the formation of the negative ion (see gold, p. 520) of a complex salt $H_2.HgCl_4$ ($= 2HCl,HgCl_2$). The red form of the sulphide is **used** in making paint (**vermilion**).

Mercuric fulminate $Hg(ONC)_2$ is obtained as a white precipitate when mercury is treated with nitric acid, and alcohol is added to the solution. It decomposes suddenly when struck, and is used in making percussion caps and detonators.

Ammono-Compounds of Mercury. — When ammonium hydroxide is added to a solution of a mercuric salt, a white substance, of a type which we have not previously encountered, is thrown down. Mercuric chloride gives $Hg(NH_2)Cl$, commonly called "infusible white precipitate," or **ammono-basic mercuric chloride.**

$$HgCl_2 + H.NH_2 + NH_3 \rightarrow Hg(NH_2)Cl + NH_4Cl.$$

The action is similar to an hydrolysis which gives a basic salt: $HgCl_2 + H.OH \rightarrow Hg(OH)Cl + HCl$, excepting that ammonia $H.NH_2$ plays the part of the water. Water gives aquo-basic salts. When liquid ammonia is the solvent, ammono-basic salts are produced. In a few cases, as here, an ammono-basic salt is obtained even when water is present. The study of reactions in liquid ammonia solutions by E. C. Franklin has led to the discovery of a large number of new and most interesting substances.

Mercuric nitrate $Hg(NO_3)_2$ and ammonium hydroxide give an insoluble **ammono-basic mercuric nitrate,** $Hg{=}N{-}HgNO_3$ which is more basic than the foregoing:

$$2Hg(NO_3)_2 + H_3.N + 3NH_3 \rightarrow Hg_2(N)NO_3 + 3NH_4NO_3.$$

When calomel is treated with ammonium hydroxide, it turns into a black, insoluble body. This is a mixture of free mercury, to which it owes its dark color, and "infusible white precipitate," $Hg + Hg(NH_2)Cl$. To this reaction calomel owes its name (Gk. καλομέλας, beautiful black). Mercurous nitrate gives a black, insoluble mixture, $2Hg + Hg_2(N)NO_3$.

Analytical Reactions of Mercury Compounds. — The two ionic forms of the element, mercurous-ion Hg^+ and mercuric-ion Hg^{++}, are both colorless. Their chemical behavior is entirely different. Both give the black sulphide HgS, which is insoluble in acids and other solvents of mercury salts. Mercurous-ion gives the insoluble, white chloride, the black oxide, and a black mixture with ammonium hydroxide. Mercuric-ion gives a soluble chloride, a yellow, insoluble oxide, and a white precipitate with ammonium hydroxide. The behavior with stannous chloride (p. 534) is characteristic. With potassium iodide the two ions behave differently (p. 534). More active metals displace mercury from all compounds. Copper is used as the displacing metal, in testing for Hg^+ or Hg^{++}, because the silvery mercury is easily seen on its surface.

Salts of mercury are volatile. When heated in a tube with sodium carbonate, they give a sublimate of metallic mercury.

THE RECOGNITION OF CATIONS IN QUALITATIVE ANALYSIS

"Wet-way" analysis consists in recognizing the various positive and negative ions present in a solution (p. 436). In discussing hydrogen sulphide (p. 273), it was stated that the sulphides might be divided into three classes, according to their behavior towards water and acids. Now these differences furnish us with a basis for distinguishing the cations present in a solution.

The following plan, taken in conjunction with the statements in the context, shows how a single cation may be identified, and how, when several cations are present, a separation preparatory to identification may be effected. What will be said applies only to the case of a *solution* containing salts like the chlorides, nitrates, or sulphates of one or more cations, and leaves the oxalates, phosphates, cyanides, and some other salts, out of consideration.

Group 1. — Add, first, **hydrochloric acid,** to find out whether cations giving insoluble chlorides are present. Argentic, mercurous, and plumbic salts give the white **$AgCl$, $HgCl$,** and **$PbCl_2$,** respectively (*cf.* p. 164). Filtration eliminates the precipitate, if there is any.

Group 2. — A free, active acid being now present, **hydrogen sulphide** is led into the solution. The sulphides insoluble in active acids, namely, **HgS, CuS, PbS, Bi_2S_3, CdS, As_2S_3, Sb_2S_3, SnS, SnS_2,** are therefore thrown down. The first four are black or brown, the next two and the last are yellow, and the remaining two are orange and brown respectively. A dark-colored substance will naturally obscure one of lighter color, if more than one is present. Filtration again eliminates the precipitate.

This group is easily subdivided. Any or all of the last four sulphides will pass into solution when warmed with yellow ammonium sulphide, for they give *soluble* complex sulphides (*q.v.*). The first five sulphides, or any of them, will be unaffected. On the other hand, these five sulphides, with the exception of HgS, will interact with hot nitric acid (p. 531). Other reactions are then used to distinguish between, or, if there is a mixture, to separate, the members of the sub-groups.

Group 3. — The solution (filtrate) is now neutralized with ammonium hydroxide, and **ammonium sulphide** is added. Some **ammonium chloride** is also used, to prevent the precipitation of magnesium hydroxide (p. 525), which, in any event, would be incomplete. The sulphides which are insoluble in water, and are not hydrolyzed by it, now appear. They are **FeS, CoS, NiS,** all black, **MnS** and **ZnS,** which are pink and white respectively. There are precipitated also the hydroxides of chromium and of aluminium, **$Cr(OH)_3$** and **$Al(OH)_3$**, because their sulphides are hydrolyzed by water.

Group 4. — After filtration, **ammonium carbonate** is added, and precipitates the remaining metals whose carbonates are insoluble, **$BaCO_3$, $SrCO_3$, $CaCO_3$,** with the exception of magnesium (p. 526).

By addition of **ammonium phosphate** *to a portion* of the filtrate, magnesium, if present, now comes out in the form **NH_4MgPO_4**. There remain in solution only salts of **potassium, sodium,** and **ammonium.** Since only ammonium compounds and other substances which can be volatilized have been added, evaporation and ignition of the residue leaves the salts of the two metals. Salts of ammonium must be sought in a fresh sample by the usual test (p. 345).

Exercises. — 1. Why should we expect ammonium sulphide solution to precipitate magnesium hydroxide, and why does it not do so?

2. What volume of air is required to oxidize one formula-weight of zinc sulphide to ZnO and SO_2, and what volume of sulphur dioxide is produced? Is the gaseous product more or less diluted with nitrogen than when pure sulphur is burned, and by how much?

3. Make equations showing, (*a*) the effect of heating zinc chloride with cobalt nitrate $Co(NO_3)_2$ in the Bunsen flame (p. 529), (*b*) the action of hydrogen sulphide on sodium zincate, (*c*) the actions of concentrated nitric acid and of concentrated sulphuric acid on mercury.

4. What kind of salts might take the place of sodium acetate in the precipitation of zinc sulphide (p. 530)? Give examples.

5. Why do none of the salts of the elements in this family give recognizable effects with the borax bead?

CHAPTER XXXIX

ELECTROMOTIVE CHEMISTRY

We have seen that many chemical changes are accompanied by a liberation of energy. If no special arrangement is made, the energy is always liberated in the form of heat, light, and mechanical energy. In changes involving ionogens, however, the energy can be secured in the form of electricity. Since the change sets an electric current in motion, the subject is called **electromotive chemistry.** A knowledge of this branch of the science is essential for understanding the numerous commercial applications of electricity in chemistry. It also furnishes us with a simple method for measuring chemical affinity in ionic reactions.

Units of Electrical Energy. — Two different units are required for defining a quantity of electrical energy. One of these is the **quantity of electricity,** which is expressed in **coulombs** (p. 237). The other is the **electromotive force** (E.M.F.) of a current, or the **difference in potential,** if a current is not flowing, or the flow is not being considered. This is measured in **volts.** It will be recalled that in electrolysis equal quantities of electricity liberate equivalent weights of the component ions (Faraday's law, p. 231). We shall see, however, that with different substances, different differences in potential (voltages) are required to produce the decomposition. A quantity of electrical energy, used or produced, is expressed by the product of the two factors:

No. of coulombs × No. of volts = Quant. of elect. energy (in **Joules**).

If we consider the time occupied by the process, the **rate** at which the electricity flows is expressed in **amperes.** One coulomb per second is one ampere. Hence:

No. of amperes × No. of volts = Joules per sec. = **Watts.**

The kilowatt is 1000 watts. The horsepower is 746 watts.

An illustration will show the meaning of this relation. If a 50-watt (16-candle power) incandescent lamp is used on a 110-

volt circuit, by substituting these values in the equation we perceive that such a lamp must carry about 0.5 amperes, or one coulomb every two seconds. If, with the *same* voltage, we wanted a lamp to carry more electricity per second, we should have to reduce the resistance of the lamp, say, by shortening the filament, or using a thicker one. Evidently, the number of such lamps required to consume one horsepower would be 736/50, or between 14 and 15 lamps. Again, to decompose one molecular weight of hydrochloric acid (36.5 g.) 96,540 coulombs (p. 237) are required, and an E.M.F. of at least 1.83 volts (see p. 548). The electrical energy needed is therefore $96,540 \times 1.83 = 176,670$ joules. If this were to be accomplished by the current from a 110-volt direct-current lighting circuit, passing through a 50-watt lamp in series with the electrolytic cell, the time required (x seconds) would be given by: 50 joules per sec. $\times\ x$ secs. $= 176,670$ joules, where $x = 3533$ seconds, or about 59 minutes.

The factors of electrical energy (volts and amperes) are easily measured when electricity is produced, and are easily provided according to any specification when electricity is to be used. Hence, it is much easier to study the relations between chemical change and this form of energy than between the same change and the heat or any other form of energy which, under other conditions, it might produce. Electrochemistry is, therefore, in many ways better understood, and easier to handle than are other branches of chemistry involving energy.

Some Reactions that can be Used to Furnish Electricity. — A few illustrations of the kinds of reactions which can easily be carried out in cells, so as to furnish an electric current instead of heat, may be classified thus:

Combination cells, such as one in which zinc (or some other active metal) and bromine are the reacting substances. If zinc be placed in bromine-water (or with pure bromine), we obtain zinc bromide:

$$Zn + Br_2 \rightarrow ZnBr_2, \quad \text{or} \quad Zn^{\circ} + 2Br^{\circ} \rightarrow Zn^{++} + 2Br^{-}.$$

Displacement cells, such as one with cupric sulphate solution and a metal more active than copper (*e.g.*, Mg, Al, Zn, or Fe), and able to displace (p. 260) this element:

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu, \quad \text{or} \quad Zn^{\circ} + Cu^{++} \rightarrow Zn^{++} + Cu^{\circ}.$$

A non-metal may also be displaced:

$$2KI + Br_2 \rightarrow 2KBr + I_2, \quad \text{or} \quad I^- + Br^0 \rightarrow I^0 + Br^-.$$

Oxidation cell, such as one in which ferrous chloride $FeCl_2$ or stannous chloride $SnCl_2$ is oxidized by chlorine-water, giving $FeCl_3$ or $SnCl_4$:

$$SnCl_2 + Cl_2 \rightarrow SnCl_4, \quad \text{or} \quad Sn^{++} + 2Cl^0 \rightarrow Sn^{++++} + 2Cl^-.$$

Concentration cells, or cells in which the same substance in two different concentrations is used.

The Arrangement of the Cell. — Every cell has one striking characteristic. If the pairs of substances mentioned in the last section are *placed together,* they interact and *heat* is produced. There is no way to avoid the action, and the liberation of the energy as heat, if the substances come in contact. **If, therefore, all the energy is to be obtained as electrical energy, the substances must be prevented from coming in contact with one another.** Paradoxical as it may seem, it is easily possible to obtain the electricity, and yet fulfill this essential condition. The plan in all cells is to place the one substance in or round one pole, and the other substance in or round the other pole, and to separate the substances by a porous partition, or some equivalent arrangement.

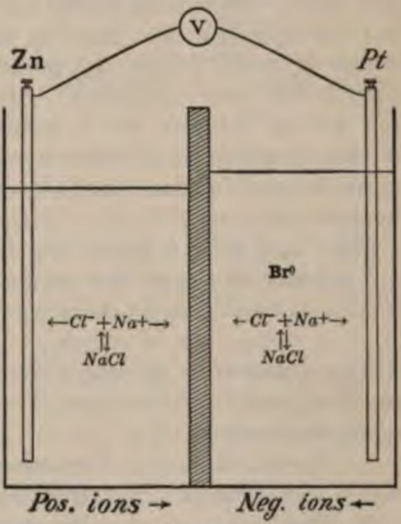


FIG. 122.

Suppose that it is the first of the above-mentioned actions that is to be used — the action of zinc and bromine. The **active substances are arranged** as follows: The pole on the left (Fig. 122) is metallic zinc. The solution on the right contains the bromine. The porous partition in the center is permeable by migrating ions, but hinders the mere diffusion of the dissolved bromine towards the zinc, and so prevents direct interaction with liberation of heat.

Now, to enable the cell to operate, **inactive, conducting substances must be added** to complete the arrangement. A pole is added on the right, a conducting solution is placed to the left of the partition, and a wire must connect the two poles. The wire may connect the poles through a voltmeter, so that the E.M.F. produced may be measured. Also, since bromine-water is a poor conductor, a well-ionized salt must be present along with the bromine. The substances used for these purposes must be inactive. For example, the pole on the right must be a conductor, but its material must not interact chemically with the bromine or with the salt. A rod of carbon or a platinum wire will serve the purpose. A more active metal, such as copper, could not be used, because it would combine with the bromine. Again, common salt or sodium nitrate may be mixed with the bromine, because it will not interact with bromine or carbon or platinum. Still again, the solution added on the left must be one which will not act upon the zinc pole, or upon the solution on the right, which it meets inside the porous partition. Common salt or niter fulfills these conditions. An acid could be used on the right, but not on the left, for it would interact with the zinc. The reader should make a different selection of inactive materials, so as to become familiar with the reasoning involved in the choice in each case.

Note that in each figure, the symbols for the **active substances** are in **black-face** type, the products are in Roman type, and the *inactive* materials are in *italic* type.

The Operation of the Cell. — When the cell has been assembled, and the wires have been connected, the following phenomena are observed:

1. The zinc begins to form zinc ions, $\mathbf{Zn} \rightarrow Zn^{++}$, an operation which leaves the pole negative (Fig. 123).
2. The bromine molecules nearest their pole touch this pole, become bromide ions, $\mathbf{Br_2} \rightarrow 2Br^-$, and leave on the pole a positive charge.
3. Since one pole is negative and the other positive, a current flows through the wire.

4. The new positive ions (Zn^{++}) round the left pole (anode) attract *all* the negative ions in the cell, and cause them to migrate towards the left so as to keep all parts of the solution neutral.

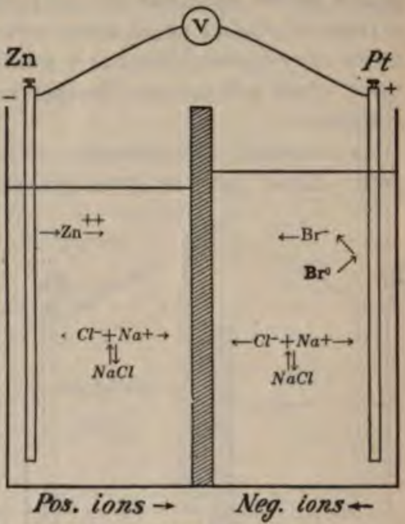


Fig. 123.

5. The new negative ions on the right (Br^-) similarly attract *all* the positive ions in the cell, and cause them to drift slowly towards the right pole (cathode).

6 (Very important). It will be seen that the zinc and the bromine **become ionized at a distance from one another and do not actually combine.** The slow migration of the Zn^{++} and Br^- ions will, of course, after some hours or days, bring some of these ions together in or near the partition, and some molecules will be formed. But this operation produces no electrical energy —it only gives out or absorbs heat (p. 255). It is not an essential part of the operation of the cell. **The chemical change which produces the current is the ionization of the two elements, separately.** The term combination cell is, therefore, misleading. The cell, as a source of electrical energy, is concerned only with producing two kinds of ions from the elements. True, these ions, if they united, would give the product shown in the equation ($ZnBr_2$), but the union, if it ever occurred, would be without electrical effect. It is clear that, since there is sodium chloride (or some other ionogen) in all parts of the cell, molecules are ionizing, and ions are combining, continually, throughout the whole system. Thus, on the left some zinc chloride molecules are formed and on the right some sodium bromide molecules, and eventually near the center some zinc bromide molecules. But these reactions occur in *every* solution containing ionogens, without giving any current. In a cell, the only reactions which contribute materially to the current are those taking place at the surfaces of the poles.

A Displacement Cell. — In a similar way, a cell using metallic zinc and cupric sulphate solution may be arranged (Fig. 124). The zinc forms one pole, and the cupric sulphate solution *must be placed on the other side* of the partition. For inactive materials, a plate of copper or of some metal below copper in the activity series may be used, and any solution (such as zinc chloride solution) which will interact neither with the zinc nor with the cupric sulphate.

In following the operation of the cell, we may start at either pole. Thus, the zinc gives zinc-ion $\mathbf{Zn}^0 \rightarrow Zn^{++} + 2\ominus$. The wire becomes negatively charged. The cupric-ion is discharged on the other pole $\mathbf{Cu}^{++} \rightarrow Cu^0 + 2\oplus$, rendering it positive. All the positive ions in the cell migrate towards the right pole (cathode). All the negative ions migrate towards the left pole (anode), since positive ions are being formed on the left and are disappearing on the right.

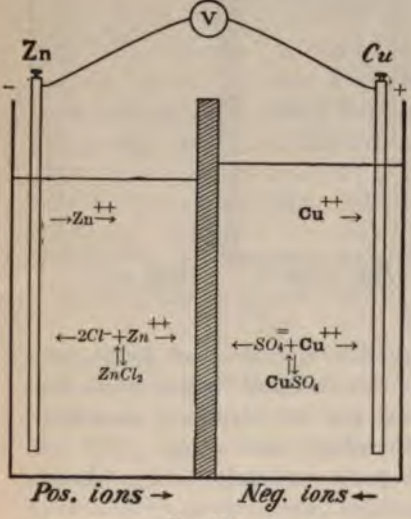


Fig. 124.

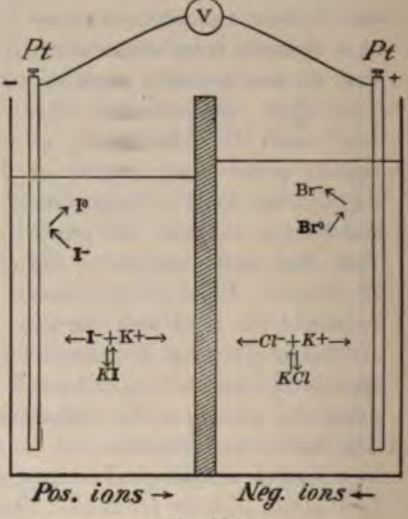


Fig. 125.

When bromine displaces iodine, the cell may be arranged as in Fig. 125. The iodine liberated dissolves in the potassium iodide solution and, with starch emulsion present, its formation can be detected in a few seconds.

The Oxidation Cell. — The arrangement whereby stannous-ion $\mathbf{Sn}^{++}$ is oxidized by chlorine-water to stannic-ion Sn^{++++} is shown in Fig. 126. The chlorine $\mathbf{Cl}^0$ encountering the pole becomes negatively charged, leaving the pole positive. This positive charge is shared by the whole conducting wire and, at the other pole, furnishes the positive electricity required to raise the charge of each tin ion from Sn^{++} to Sn^{++++}. Only the tin ions which *touch* the pole can acquire the charge.

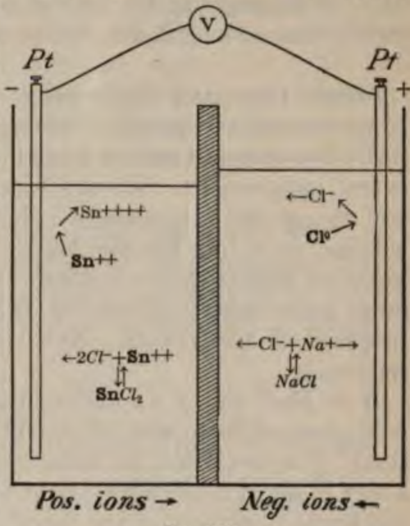


FIG. 126.

Facts Concerning all Cells. — If the wire is disconnected, the progress of the chemical action is stopped, although the difference in potential remains. The charge conferred upon a pole, such as that from the cupric ion (Fig. 124), must be conducted away, before additional charges will be transferred to it.

If a glass partition is substituted for a porous one, the cell ceases to generate electricity. The partition must permit the trans-migration of the ions, which is a necessary part of the operation of the cell.

When the circuit is closed, the changes described go on until one of the active materials is exhausted — for example, until all the cupric-ion has been deposited as copper, or until all the zinc has been consumed.

The quantity of electricity producted is 96,540 coulombs for each equivalent weight of the active materials transformed, *e.g.*, for every 65.4/2 g. of zinc consumed. The *rate* at which the electricity is produced is, in general, greater the larger the area of the poles. The amperage of a *single* cell is, in general, very low.

The E.M.F. of the cell is not changed by altering the size or shape of the poles, or by using more or less of the solutions. It *is* affected by any change in the *qualities* of the *active* materials, however. Changing the concentration (see p. 551) of the cupric-ion (Fig. 124) or of the bromine-water (Fig. 125) has an immediate effect. So has substituting one active metal for another (see p. 547), as magnesium for zinc (Fig. 123). Even hammering the metal, thus making it denser, has a slight effect.

Single Potential Differences Produced by the Metals. — If we reconsider the cells described, we shall see that there are really **two chemical actions in each cell** and that these are to some extent independent. We can leave the zinc (Fig. 123) constant, and change the concentration of the bromine or even substitute chlorine or iodine for the latter. On the other hand, we can leave the bromine-water constant, and exchange the zinc for some other active metal. Thus, the E.M.F. of every cell is really the resultant of two effects. Now, these effects can be measured, separately.

If we place zinc in a solution of zinc chloride, we find that there is at once a difference in potential between the metal and the solution! The metal has an individual tendency to become ionic — a sort of solution pressure — and to form a few ions, thus making the liquid positive and the metal negative. In reality, it is the tendency of the atoms of the metal to give up electrons (p. 235), *e.g.*, $Zn - 2\epsilon = Zn^{++}$, which is being observed. On the other hand, the ions have a tendency to deposit themselves, and a few may be deposited (taking up their electrons and becoming neutral), rendering the pole positive and the solution negative. If the former tendency (the tendency to give up electrons) is the stronger of the two (the more active metals), then a difference in potential is produced, with the solution positive. If the latter tendency is the stronger (less active metals) the solution is observed to be negative. Since raising the concentration of the metal-ions will increase the tendency to deposition and *vice versa*, it is customary to take as the standard solution, for this purpose, one in which the concentration of the metal-ions is normal (N). In the following table, the sign preceding the number is the charge of the *solution*.

POTENTIAL OF N SOLUTIONS IN CONTACT WITH METALS
(E.-M. SERIES)

K	(+ 2.6)	Fe (Fe^{++})	+ 0.2	Bi	− 0.63?
Na	(+ 2.4)	Cd	+ 0.16	Sb	− 0.71?
Ba	(+ 2.6)	Co	+ 0.05	Hg (Hg^{+})	− 0.99
Sr	(+ 2.5)	Ni	− 0.02?	Pd	− 1.03?
Ca	(+ 2.4)	Pb	− 0.12	Ag	− 1.04
Mg	+ 1.3	Sn (Sn^{++})	− 0.14	Pt	− 1.10?
Al	+ 1.0	**H**	− 0.24	Au	− 1.7?
Mn	+ 0.8	As	− 0.53		
Zn	+ 0.5	Cu (Cu^{++})	− 0.58		

Thus, opposite Mg we find +1.3. This means that when a piece of magnesium is placed in a solution of a salt of magnesium, containing normal concentration of Mg^{++}, the solution is positively charged (the metal negatively) and the difference in potential is 1.3 volts. With silver in a solution of a salt of silver, containing normal concentration of silver-ion, the solution is negative and the difference in potential is −1.04 volts.

For a hydrogen pole, a piece of palladium saturated with hydrogen (p. 57) is used. The values for the metals which decompose water with ease cannot be observed, and so calculated values are given in parentheses.

Applications: E.M.F. of a Displacement Cell. — For a cell in which one metal is going into solution and another is being deposited — like that with zinc and cupric sulphate — we can calculate from the foregoing data the E.M.F. of the cell. Zinc in normal zinc-ion solution makes the solution +0.5. Copper in normal cupric-ion solution makes the solution −0.58. The anodic and cathodic systems are here stated as if they worked against one another. The combined effect of the two is therefore the difference: $+ 0.5 - (-0.58) = 1.08$ volts.

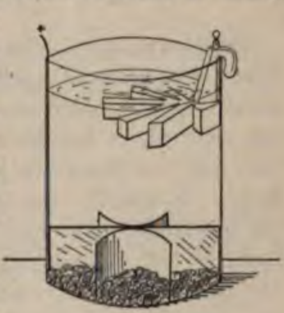


FIG. 127.

The Daniell or **gravity cell** (Fig. 127) represents this combination. The copper plate is at the bottom and the zinc is suspended above it. The cell is filled with dilute sodium chloride solution and crystals of cupric sulphate are thrown in. So long as the cell is not disturbed, the heavy, saturated solution of cupric sulphate remains at the bottom, so that no porous partition is required. The actual E.M.F. of this cell is not exactly that calculated for normal solutions, because the cupric sulphate is in saturated solution, and the concentration of the zinc-ion varies, starting at zero and increasing as the cell is used. It is, however, a little over 1 volt.

The **Weston Standard Cell** contains a pole of mercury in a saturated solution of mercurous sulphate and cadmium in contact with saturated cadmium sulphate solution. For normal solutions, the voltage would be $+0.16 - (-0.99) = 1.15$ volts. At 20° it is 1.0183 volts.

The **Clark Standard Cell** contains zinc and zinc sulphate solution in place of the cadmium. With normal solutions it would give $+0.5 - (-0.99) = 1.49$ volts. It actually gives 1.434 volts.

Single Potential Differences for Non-Metallic Ions. — The corresponding figures for the non-metals are:

I	-0.78	Br	-1.32	Cl	-1.59

Hence the cell with zinc and bromine-water (p. 541) in presence of normal concentration of the respective ions gives $+0.5 - (-1.32) = 1.82$ volts. Similarly, the cell in which bromine displaces iodine (p. 544) gives $-0.78 - (-1.32) = 0.54$ volts.

Applications: Electrolysis: Discharging Potentials. — When a solution of a salt, such as cupric chloride, is electrolyzed, copper and chlorine are liberated at the two poles. Now, when the electrolysis has made some progress, if the battery is taken out, and the wires are joined, a current, the **polarization current,** flows. Evidently, the copper and chlorine liberated in and round the electrodes have made the arrangement into a copper-chlorine battery cell. Assuming normal concentrations, the E.M.F. of the polarization current is $-0.58 - (-1.59) = 2.17$ volts. Now this counter-current is in operation during the whole electrolysis. To overcome it, and maintain the electrolysis, evidently an E.M.F. of at least 2.17 volts from the battery is required. This is called the **discharging potential** for cupric chloride.

Applications: Electrolytic Refining. — The electrolytic process for refining copper (read p. 511) can now be more easily understood. *Both* electrodes are made of copper, and the solution contains cupric sulphate. There is, therefore, no difference in potential between the plates, except a very small one, due to the fact that one plate is pure copper and the other impure. Hence a very slight E.M.F., sufficient to overcome the difference just mentioned, and to overcome the friction of the moving ions, is all that is required, and 0.5 volts is sufficient.

As regards the resulting **purification,** the anode of crude copper, which is being consumed, contains, besides copper, small amounts of less active metals like silver and gold, and of more active metals like zinc. So far as the more active metals are concerned, the cell is like one with zinc and cupric sulphate (p. 544). It would run *by itself,* without any outside current, and would actually generate a current. Hence the active metals become ionic easily, and displace cupric-ion from the solution. The less active metals, on the other hand, are not required for the transference of the electricity, since a great excess of the more active copper is available. They also require a larger E.M.F. for their ionization than does copper. Hence, they remain as metals, and drop to the bottom of the cell (sludge) as the anode of crude copper wears away.

Applications: Couples. — The fact that metallic zinc will displace hydrogen-ion from an acid, or cupric-ion from cupric sulphate solution can now be explained. The more active metals are the ones which have the greatest tendency to become ionic. Each will deprive the ions of a metal below it in the list of their electric charges:

$$Zn^0 + 2H^+ \rightarrow Zn^{++} + H_2^0\uparrow.$$
$$Zn^0 + Cu^{++} \rightarrow Zn^{++} + Cu^0\downarrow.$$

Now we have noted the facts (pp. 55, 626) that contact with a platinum wire, or the presence of impurities (other metals) in the zinc, will hasten its action. Pieces of two metals in contact with one another constitute a couple. With zinc and platinum in an acid, a current is set up, like that of a short circuited cell. The zinc becomes negative, the platinum positive, and the hydrogen is *liberated upon the platinum.* This facilitates the action because, when the platinum is absent, and the hydrogen gas, in bubbles, is liberated on the surface of the zinc, this surface is only partly in contact with the acid (H^+), and so the liberation of the hydrogen is slower.

Galvanized iron is also a couple. When rain (dilute carbonic acid) falls upon it, the zinc, being the more active metal (p. 528), is the anode and tends to become ionized (forming the carbonate). The iron is the cathode and is not affected. The carbonate, however, forms a closely adhering coating on the zinc, and so but little of this metal is actually consumed, and the material is therefore durable. On the other hand, a sheet of iron, without the zinc coating, gives ferrous carbonate which is easily oxidized to ferric hydroxide (a base too weak to give a carbonate). This forms a brittle, porous layer which does not mechanically protect the surface from further action, and so the iron is finally all oxidized. **Tin-plate** (tin on iron, a couple) is not attacked so long as the layer of tin is nowhere broken. But damaged tin-plate rusts rapidly. There, the iron is the more active metal (p. 547) and forms carbonate and then hydroxide continuously, while the tin remains unaffected.

Applications: Measurement of Affinity. — Since equal quantities of electricity bring about (or are brought about by) chemical changes in chemically equivalent weights of material, it follows that the E.-M. forces required (or produced) are proportional to the chemical affinity. Thus the activities of the metals, expressed in volts (p. 547), are accurate figures for the relative affinities of the metals, so far at least as ionic actions are concerned. In point of fact, they express also the approximate affinities of the metals in other actions (pp. 60, 531) as well. Again, by using different oxidizing agents in place of the chlorine-water (p. 545) and noting the differences in potential, we can obtain numbers representing the relative activities of various oxidizing agents towards oxidizable ions.

Concentration Cells. — If two rods of a metal (*e.g.*, tin) are placed together in the same solution of a salt of the metal (*e.g.*, stannous chloride $SnCl_2$), there is no difference in potential, because the state of both poles is in all respects the same. But, if the solution round one pole is more concentrated than that round the other, a difference in potential is produced (Fig. 128). The tendencies of the metallic tin to form ions are equal, but the pressures of the stannous ions are different, and so, when the circuit is closed, stannous ions are discharged on the tin pole in the more concentrated solution, forming long crystals of tin, and tin in equal amount from the pole in the dilute solution becomes ionic.

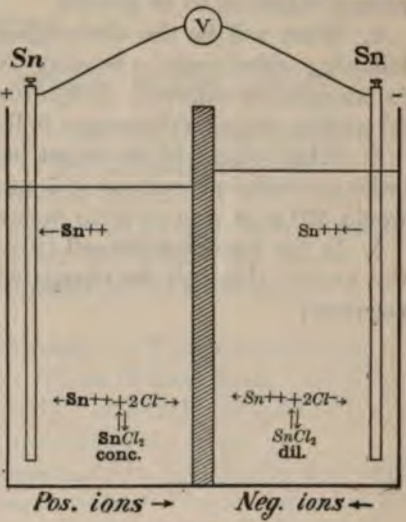


Fig. 128.

The law which formulates the relation between the two concentrations and the E.M.F. produced being known, it is possible to use the concentration cell for measuring solubilities of insoluble salts. Thus, we cannot easily measure the solubility of silver chloride by the ordinary method (p. 123), because evaporation of the solution may leave a larger mass of impurities, derived from solution of the glass, than of dissolved silver chloride. Hence, we use two poles of silver, place one in normal silver nitrate solution and the other in saturated silver chloride solution (with excess of the solid), measure the difference in potential, and calculate the ratio of the concentrations of silver-ion in the two solutions. The absolute value of that in the silver nitrate solution is known, and so the absolute value of the Ag^+ concentration in the silver chloride solution can be found. Since silver chloride is a salt (p. 242), it is very highly ionized in so dilute a solution, and the molecular concentration of silver-ion is practically equal to the total molecular concentration of silver, and therefore of silver chloride in the liquid.

Exercises. — 1. Make diagrams of the following cells, choosing with care suitable inactive substances to complete the arrangement: (*a*) chlorine-water and aluminium; (*b*) chlorine-water and ferrous chloride; (*c*) zinc and dilute sulphuric acid; (*e*) chlorine-water and potassium bromide.

2. Calculate the E.M.F. of each of the cells in Ex. 1, assuming normal solutions to be present.

3. What will be the discharging potentials of solutions of the following substances, assuming N concentrations of the ions: (*a*) manganous chloride; (*b*) hydrogen iodide; (*c*) ferrous bromide; (*e*) sodium chloride (hydrogen is liberated)?

4. What weight of zinc must be ionized every hour in a cell in order to produce a current of 5 amperes strength? For how long would 500 g. of zinc serve to maintain this current?

5. In the zinc-bromine cell (p. 543), why is the zinc pole called the anode, although its charge with respect to the platinum is negative?

CHAPTER XL

ALUMINIUM AND THE METALS OF THE EARTHS

THE chief members of the family occupying the fourth column of the periodic table are: boron (B, at. wt. 11), aluminium (Al, at. wt. 27.1), gallium (Ga, at. wt. 70), indium (In, at. wt. 115), thallium Tl, at. wt. 204), all on the right side of the column; and scandium (Sc, at. wt. 44.1), yttrium (Y, at. wt. 89), lanthanum (La, at. wt. 139), on the left side. These elements are all trivalent.

The Rare Elements of this Family. — The oxide and hydroxide of boron are acidic (p. 431). Those of aluminium ($Al(OH)_3$), gallium ($Ga(OH)_3$), indium ($In(OH)_3$), and thallium (TlO.OH) are basic, but behave also as acids towards strong bases.

Gallium and **indium** occur occasionally in zinc-blende, and were discovered by the use of the spectroscope. The former takes its name from the country (France) in which the discovery was made, and the latter from two blue lines shown by its spectrum.

Thallium is found in some specimens of pyrite and blende. It was discovered by Crookes, by means of the spectroscope, in the seleniferous deposit from the flues of a sulphuric acid factory. It received its name from the prominent green line in its spectrum (Gk. θαλλός, a green twig). It gives two complete series of compounds. In those in which it is trivalent (thallic salts), it resembles aluminium (*q.v.*). Thus, the salts of this series are more or less hydrolyzed by water. Univalent thallium recalls both sodium and silver. Thallous hydroxide TlOH is soluble, and gives a strongly alkaline solution, but the chloride is insoluble in cold water. The solutions of the thallous salts are neutral. The metal is displaced from its salts by zinc.

Of the elements on the left side of the column, **scandium,** whose existence and properties were predicted by Mendelejeff (p. 301), is the best known. The metals of the **rare earths,** of which it is one, are found in rare minerals such as euxenite, gadolinite, orthite, and monazite, which occur in Sweden, Greenland, and the United States. **Cerium** (Ce, at. wt. 140.25), **neodymium** (Nd, at. wt. 144.3), and **praseodymium** (Pr, at. wt. 140.9) occur along with **lanthanum** in cerite, a silicate of these four elements. These four are included amongst the metals of the rare earths. The compounds of many of these rare elements behave so much alike that separation is difficult. There are several with atomic weights near to that of lanthanum for which accommodation cannot easily be found in the periodic table. Ostwald has compared them to a group of minor planets such as in the solar system takes the place of one large planet.

ALUMINIUM

The Chemical Relations of the Element. — Aluminium is trivalent exclusively. Its hydroxide, like that of zinc (p. 529), is amphoteric, that is to say, it is feebly acidic as well as basic, and hence the metal forms two sets of compounds of the types $Na_3.AlO_3$ (sodium aluminate) and $Al_2.(SO_4)_3$. The salts of both series are more or less hydrolyzed by water, the former very conspicuously so. It is worth noting that the hydroxides of the trivalent metals, or metals in the trivalent condition, such as $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$, are all distinctly less basic than are those of the bivalent metals such as $Zn(OH)_2$, $Cd(OH)_2$, $Fe(OH)_2$, $Mn(OH)_2$. Aluminium does not enter into complex anions or cations, and is too feebly base-forming to give salts like the carbonate or sulphide.

Occurrence. — Aluminium is found very plentifully in combination, coming next to oxygen and silicon in this respect. The felspars (such as $KAlSi_3O_8$), the micas (such as $KAlSiO_4$), and kaolin (clay) $H_2Al_2(SiO_4)_2,H_2O$ are the commonest minerals containing it. Since the soil has been formed largely by the weathering of minerals like the felspars, clay and other products of the decomposition of such minerals constitute a large part of it. Cryolite is a double fluoride $3NaF,AlF_3$. Various forms of the oxide and hydroxide are also found.

Preparation and Physical Properties. — The metal is now made on a large scale by electrolysis of the oxide Al_2O_3 dissolved in a bath of molten cryolite (m.-p. 1000°), a process invented by C. M. Hall (1886). The operation is conducted in cells (5 × 3 feet, or larger), the carbon linings of which form the cathodes (Fig. 129). The anodes are rods of carbon which combine with the oxygen as it is liberated. The molten metal (m.-p. 659°) sinks to the bottom of the cell and is drawn off periodically, while fresh portions of the oxide are added from time to time. The oxide is made from bauxite (see below), and must be free from oxide of iron and other impurities, as the metal cannot be purified commercially. The current (E.M.F. 5–6 volts) maintains the temperature of the molten materials, and causes the decomposition. In 1866 aluminium cost $250–750 (£50–150) per kilogram. In 1883 the whole production was about 40 kilos. In 1913 the United States alone consumed 35 million kilos, costing about 50 cents (2/–) per kilo.

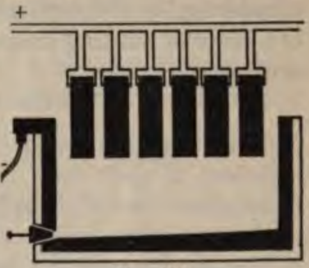


Fig. 129.

The metal melts at 658.5°, but is not mobile enough to make castings. It is exceedingly light (sp. gr. 2.6), and in tensile strength excels the other metals, with the exception of iron and copper. It is malleable, and the foil is taking the place of tin foil for wrapping foods. It has a silvery luster, and tarnishes very slightly, the *firmly adhering* film of oxide first formed protecting its surface. Although, comparing cross-sections, it is not so good a conductor of electricity as is copper, yet *weight for weight* it conducts better. It is difficult to work on the lathe or to polish, because it sticks to the tools, but the alloy with magnesium (about 2 per cent) called **magnalium** has admirable qualities in these respects. **Aluminium bronze** (5–12 per cent aluminium with copper) is easily fusible, has a magnificent golden luster, and possesses mechanical and chemical resistance exceeding that of any other bronze. The metal and its alloys are used for making cameras, opera-glasses, cooking utensils, and other articles requiring lightness and strength, as well as for the transmission of electricity. The powdered metal, mixed with oil, is used in making a silvery paint.

Chemical Properties. — The metal displaces hydrogen from hydrochloric acid very easily. It displaces hydrogen also from boiling solutions of the alkalies, forming aluminates:

$$2Al + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2.$$

In consequence of its very great affinity for oxygen, aluminium displaces from their oxides the metals below magnesium in the E.-M. series. Thus, when a mixture (**thermite**) of aluminium powder and ferric oxide is placed in a crucible and ignited by means of a piece of burning magnesium ribbon, aluminium oxide and iron are formed:

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe.$$

The very high temperature (about 3000°) produced by the action is sufficient to melt both the iron (m.-p. 1530°) and the oxide of aluminium (m.-p. 2050°). The products, not being miscible, separate into two layers. This very simple method of making pure specimens of metals like chromium, uranium, and manganese, whose oxides are otherwise hard to reduce, is called by Goldschmidt, the inventor, **aluminothermy.** By preheating the ends of steel rails with a gasoline torch, firing a mass of thermite in a crucible above the joint, and allowing the iron to flow into the joint, perfect welds are made. In the same way, large castings, like propeller shafts, when broken, can be mended. The sulphides, such as pyrite, are reduced with like vigor by aluminium.

The largest part of the aluminium of commerce is used by steelmakers. When added in small amount (less than 1 : 1000) to molten steel, it combines with the gases, and gives sound ingots free from blow holes.

Aluminium Chloride $AlCl_3$. — If the metal or the hydroxide is treated with hydrochloric acid, and the solution is allowed to evaporate, the **hydrated chloride** $AlCl_3,6H_2O$ is formed. When heated, this hydrate is completely hydrolyzed, hydrochloric acid is given off, and only the oxide remains. The **anhydrous chloride** $AlCl_3$ is made by passing dry chlorine over aluminium. Since it sublimes as a white crystalline solid without melting, when thus prepared it is vaporized and condenses in a cool part of the tube. It fumes when exposed to moist air on account of the hydrogen chloride produced by hydrolysis, and only with excess of hydrochloric acid does it give a clear solution free from basic salts.

Aluminium Hydroxide and the Aluminates. — When an alkali is added to a solution of a salt of aluminium, the **hydroxide** $Al(OH)_3$ is precipitated in gelatinous form. It loses water gradually when dried, forming no intermediate hydroxides, until Al_2O_3 remains. Natural forms of this substance are hydrargyllite $Al(OH)_3$ ($= Al_2O_3,3H_2O$), bauxite $Al_2O(OH)_4$ ($= Al_2O_3,2H_2O$), which always contains ferric oxide, and diaspore $AlO.OH$ ($=Al_2O_3,$-H_2O).

Commercially, the hydroxide is made by heating bauxite with dry sodium carbonate, and extracting the sodium metaluminate with water:

$$Al_2O(OH)_4 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2 + 2H_2O.$$

The iron, present as an impurity, remains, as ferric oxide, undissolved. The hydroxide is then precipitated by passing carbon dioxide through the solution:

$$2NaAlO_2 + CO_2 + 3H_2O \rightarrow Na_2CO_3 + 2Al(OH)_3.$$

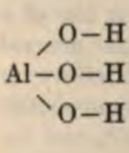
Aluminium hydroxide, being amphoteric, interacts both with acids and with bases, and is, therefore, like zinc hydroxide (p. 531), ionized both as a base and as an acid. It interacts only slightly with ammonium hydroxide, because this substance is too feebly basic, but, from the solution in the active alkalies, the **aluminates** $Na_3.AlO_3$, $Na.AlO_2$, and $K.AlO_2$, can be obtained in solid form. The aluminates are largely hydrolyzed by water:

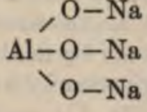
$$NaAlO_2 + 2H_2O \rightleftarrows NaOH + Al(OH)_3.$$

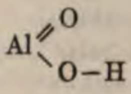
When calcium chloride is added to a solution of sodium aluminate, the insoluble **calcium metaluminate** is deposited:

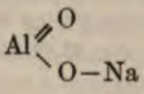
$$2NaAlO_2 + CaCl_2 \rightarrow Ca(AlO_2)_2 + 2NaCl.$$

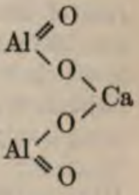
The relations of these various substances are shown by the following formulæ:











A number of insoluble metaluminates, such as spinelle $Mg(AlO_2)_2$, and gabnite $Zn(AlO_2)_2$, are found in nature. They contain bivalent metals in place of the calcium in the last-named compound.

Aluminium Oxide Al_2O_3. — The oxide (**alumina**) is manufactured by heating the pure hydroxide made from bauxite (see above). It is found in nature in pure form as corundum. This mineral is only one degree less hard than the diamond. *Emery* is a common variety, contaminated with ferric oxide, and was widely used as an abrasive, until largely displaced by carborundum. The ruby is pure aluminium oxide tinted by a trace of a compound of chromium, while the sapphire is the same material colored with aluminates of iron and titanium. It is said, however, that the same tint is conferred upon colorless corundum by exposure to the influence of salts of radium. By ingenious methods of fusing the oxide, "synthetic" sapphires and rubies are now made in large quantities. **Alundum,** a refractory material for crucibles, is made by heating objects made of the oxide in the electric furnace until a small proportion of the material is melted.

Aluminium Sulphate: The Alums. — **Aluminium sulphate** $Al_2(SO_4)_3,18H_2O$ is prepared by treating either bauxite, or the pure hydroxide made from bauxite, or pure clay (kaolin) with sulphuric acid. In the latter case the insoluble residue of silicic acid is removed by filtration:

$$H_2Al_2(SiO_4)_2 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 2H_2SiO_3 + 2H_2O.$$

The solution of the sulphate is acid in reaction. It crystallizes in leaflets which, when the source was clay or bauxite, have a yellow tinge due to the presence of iron as an impurity. The salt is used as a source of precipitated aluminium hydroxide in paper-making, water purification, and dyeing.

When sulphate of potassium solution is added to a strong solution of aluminium sulphate, octahedral crystals of potash alum (see below) are deposited. This is a double salt, and is one of a large class known as the **alums.** The alums have the general formula $M_2{}^{I}SO_4,M_2{}^{III}(SO_4)_3,24H_2O$, and may be made as above by using a sulphate of a univalent metal with one of a trivalent metal. Thus, for M^{I} we may use K, NH_4, Rb, Cs, and Tl^{I}, and for M^{III}, Al, Fe^{III}, Cr^{III}, Mn^{III}, and Tl^{III}. All the alums crystallize in octahedra.

Potassium-aluminium sulphate $K_2SO_4,Al_2(SO_4)_3,24H_2O$, ordinary alum, is made from aluminium sulphate. It is also prepared by heating alunite, a basic alum found near Rome and in Hungary, and extracting the product with water. The alunite $KAl_3(OH)_6(SO_4)_2$ leaves an insoluble residue of the hydroxide, mixed with ferric oxide which is present as an impurity:

$$2KAl_3(OH)_6(SO_4)_2 \rightarrow K_2SO_4,Al_2(SO_4)_3 + 4Al(OH)_3.$$

The hydrated salt melts at 90°. An aqueous solution of this salt, or of sodium phosphate (p. 464), is used for fireproofing draperies. The crystals deposited in the fabric melt easily, and the fused material protects the fibers from access of oxygen. When heated more strongly alum loses its water of hydration, together with some sulphur trioxide, and leaves a slightly basic, anhydrous salt known as **burnt alum.** Potash-alum and ammonium-alum are more easily freed from impurities (*e.g.*, compounds of iron) by recrystallization than is aluminium sulphate, and the alums are therefore used instead of the latter in medicine, in dyeing delicate shades, and to replace cream of tartar in baking powder (p. 463). In the last case, the reaction

$$K_2SO_4,Al_2(SO_4)_3,24H_2O + 6NaHCO_3 \rightarrow K_2SO_4 + 3Na_2SO_4 \\ + 2Al(OH)_3 + 6CO_2 + 24H_2O$$

liberates carbon dioxide by hydrolysis of the aluminium carbonate.

Hydrolysis of Aluminium Carbonate. — The foregoing action, and others discussed above (p. 557), show that the carbonate is *completely* hydrolyzed:

$$Al_2(CO_3)_3 + 6H_2O \rightleftarrows 2Al(OH)_3 \downarrow + 3H_2CO_3 \rightarrow 3H_2O + 3CO_2 \uparrow.$$

It will be seen that this may be due only *in part* to the feebly basic qualities of the hydroxide. If the hydroxide were not precipitated, it would cause some reversal of the action, and *some* of the carbonate would remain. The insolubility of one product explains also other cases of the complete hydrolysis of salts (*e.g.*, ammonium silicate p. 429 and next section).

Aluminium Sulphide Al_2S_3. — This salt is most easily obtained by mixing pyrite with aluminium powder and igniting with magnesium ribbon (p. 556):

$$3FeS_2 + 4Al \rightarrow 2Al_2S_3 + 3Fe.$$

It forms a grayish-black solid, and is decomposed by water, as is magnesium sulphide, giving the hydroxide and hydrogen sulphide. On this account, the sulphide, like magnesium sulphide (p. 538), cannot be formed by precipitation in presence of water. Thus, ammonium sulphide with a salt of aluminium, in solution, gives a precipitate of aluminium hydroxide:

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O \rightarrow 2Al(OH)_3 \downarrow + 3(NH_4)_2SO_4 + 3H_2S.$$

Coagulation Method of Purifying Water: Sizing Paper.— When aluminium hydroxide is formed, it gives first a colloidal suspension, which coagulates to a gelatinous precipitate. When this precipitate is produced in water used for domestic purposes, and containing fine, suspended matter, the gelatinous material causes the fine particles to collect into larger ones which settle rapidly, and permits the use of relatively small settling ponds. These larger particles enclose also practically all the bacteria. If the water is slightly hard, crude aluminium sulphate, alone, is added:

$$3Ca(HCO_3)_2 + Al_2(SO_4)_3 \rightarrow 3CaSO_4 + 2Al(HCO_3)_3, \qquad (1)$$
$$Al(HCO_3)_3 + 3H_2O \rightarrow Al(OH)_3 \downarrow + 3H_2CO_3. \qquad (2)$$

If the water is very soft, a little lime $Ca(OH)_2$ is added. The few remaining bacteria are destroyed by later addition of bleaching powder or chlorine-water (p. 312).

In some localities crude ferrous sulphate, obtained as a by-product in cleaning iron, is cheaper, and is employed instead. The lime precipitates ferrous hydroxide $Fe(OH)_2$. This is quickly oxidized to colloidal ferric hydroxide $Fe(OH)_3$, which coagulates the suspended matter.

Aluminium hydroxide is employed also in **sizing** cheaper grades of **paper** (p. 402), an operation required to prevent the absorption and consequent spreading of the ink. For writing-paper, gelatine solution is employed. In making printing-papers, rosin soap (made by dissolving rosin in caustic soda) is mixed with the paper-pulp, and aluminium sulphate is added. The rosin and aluminium hydroxide are precipitated in the pulp, perhaps in feeble combination, and pressing between hot rollers afterwards melts the former and gives a surface to the paper.

Delicate cloth goods are rendered waterproof by saturating them with aluminium acetate solution and then steaming them to promote hydrolysis. The aluminium hydroxide is thus precipitated in the capillaries of the cotton or linen and renders them non-absorbent:

$$Al(CO_2CH_3)_3 + 3H_2O \rightleftarrows Al(OH)_3 + 3HCO_2CH_3.$$

Kaolin and Clay: Earthenware and Porcelain. — By the action of water and carbon dioxide upon granite, and other rocks containing felspar $KAlSi_3O_8$, the potash is slowly removed, and the compound is changed largely into a hydrated orthosilicate $H_2Al_2(SiO_4)_2,H_2O$. When pure, it forms **kaolin** or china clay, a white, crumbly material. When washed away and redeposited, it usually acquires compounds of iron, the carbonates of calcium and magnesium, and sand (silica), becoming common clay. Ocher, umber, and sienna are clays colored with oxides of iron and manganese. Fuller's earth is a purer variety.

The plasticity of clay, a property connected with the colloidal nature of the kaolin, enables it to be fashioned into various shapes. When heated, it shrinks and becomes a hard, solid, porous mass, and does not melt. These two properties enable us to use it in making bricks, pottery, and porcelain. The presence of calcium and magnesium compounds makes the clay more fusible, because it permits the formation of fusible silicates of these metals. **Bricks** and **tiling** for roofs and drains are made of common clay and, when red, owe their color to oxide of iron Fe_2O_3. The firing is done with fuel gas in ovens or kilns of brickwork. To glaze drain pipes and some bricks, salt is thrown into the kiln. The water vapor, at a red heat, hydrolyzes the salt, hydrogen chloride is set free, and the sodium hydroxide gives with the clay a fusible sodium-aluminium silicate which fills the surface pores. Clay for fire brick (infusible) must contain silica, but no lime.

China and **porcelain** are made from pure clay, free from iron, to which a little of the more fusible felspar is added. After the first firing, the articles are porous (bisque), and must be covered with a glaze. A paste of finely ground felspar and silica, sometimes containing lead oxide, is spread on the surface, and the articles are fired again, at a higher temperature. Colored decorations are added by means of suitable materials, mainly oxides of metals which give colored silicates. The third firing causes these oxides to interact and fuse with the glaze.

The Schwerin process for separating ferric oxide Fe_2O_3 from clay, so that white porcelain may be obtained, is now used on a large scale and affords an interesting application of the properties of colloidal suspensions (p. 417). When the impure clay is suspended in water, the particles of ferric oxide are positively charged and those of the clay are negative. By inserting plates connected with the dynamo in the trough, the clay particles are caused to drift towards the positive plate and the ferric oxide towards the other, so that, when the liquid from the positive end is allowed to settle, pure clay is obtained.

In making bricks, in some cases, advantage is taken of the fact that negative colloids, such as clay, become more strongly negative in presence of a trace of free alkali. Thus, when a trace of sodium hydroxide is added to clay slip, the particles repel one another more strongly, the cohesion which causes the plasticity is reduced, and the clay can be poured into molds. This avoids diluting the clay with water, which would only have to be driven out again, with great waste of heat, in the firing.

Cement. — Cement is made by heating limestone $CaCO_3$, and clay $HAlSiO_4$, or a natural rock containing both materials in the right proportions. Such a rock, made into cement by volcanic heat, was quarried by the Romans near Naples and elsewhere, and its capacity for hardening even under water was utilized by them. Blast-furnace slag, when pulverized and heated with limestone, has been found to yield an excellent quality of cement, and a valuable use has thus been found for what was formerly an annoying encumbrance. The mixture, or pulverized natural rock, is moistened and fed slowly in at the upper end of an inclined (6°) revolving cylinder of iron (20 to 45 by 2 meters). The motion continually turns over the thin layer, and exposes every particle to the heat of the air-blast, charged with pulverized coal, burning in the interior. The product slides out in a continuous stream at the lower end, and is pulverized by steel balls in a ball mill.

Cement is held to be a mixture of calcium silicate and calcium aluminate. The former is simply a filler. The latter is hydrolyzed by the water:

$$Ca_3(AlO_3)_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2H_3AlO_3.$$

The calcium hydroxide slowly crystallizes, connecting the particles of the calcium silicate. The aluminium hydroxide fills the interstices and renders the whole compact and impervious.

Ultramarine. — Formerly, pulverized *lapis lazuli*, a rare mineral of beautiful blue color, was used by artists as a pigment. Gmelin (1828) found a way of making it artificially. A mixture of kaolin, sodium carbonate, sulphur, and charcoal is heated until a green mass is obtained. This mass is then pulverized and heated with more sulphur. The product is used as laundry blueing, in making blue-tinted paper, and with oil in making paint. It is also added in small amount to correct the natural yellow tint of linen, starch, sugar (p. 405), and paper-stock. By varying the mode of heating, without altering the composition, various colors from green to reddish violet can be obtained. No pure colored substance can be extracted from it. The variety of colors is due to different degrees of colloidal dispersion of some substance suspended in the solid, just as gold, which is pale yellow in mass, gives colloidal suspensions (p. 416) of different colors (red, purple, or blue) according to the fineness of the particles (*cf.* p. 494).

Dyeing. — The problem of the dyer is to confer the desired color upon a fabric made, usually, of cotton, linen, wool, or silk, and to do this in such a way that the dye is fast to (*i.e.*, is not removed or destroyed by) rubbing and light, and often, also, to washing with soap. To understand the means by which this is achieved, it must be noted that cotton and linen consist of smooth hollow fibers (Fig. 130*A*) of the composition of cellulose $(C_6H_{10}O_5)_x$. Wool is made of hollow fibers, with a scaley surface (*B*) and silk of solid filaments, but these are composed of proteins (p. 422). Now, the proteins are much more active chemically than is cellulose, and also, as colloidal materials, seem to have a much greater tendency to adsorb other substances than has cellulose. Hence, accidental stains on wool or silk are much less often

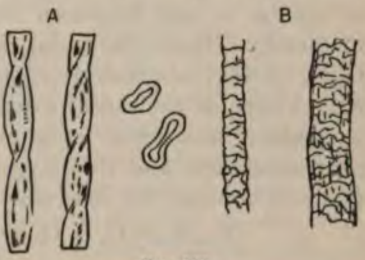


FIG. 130.

removable than are those on cotton, and when samples of the three materials are dipped in a solution of a dye, the first two are permanently dyed, while from the last most dyes can be completely washed out with water.

Three modes of dyeing may be mentioned:

1. **Insoluble Dyes.** If the colored body can be produced by *precipitation*, after the solution has filled the capillary and wall of every fiber of the goods, then, if the dye is sufficiently insoluble, it is mechanically imprisoned in every fiber and cannot be washed out. This plan may be applied to any kind of goods. For example, if cotton, silk, or wool is first boiled in a solution of lead acetate, and is then soaked in a boiling solution of potassium chromate, it is dyed a brilliant, permanent yellow. Lead chromate is the colored body:

$$Pb(CO_2CH_3)_2 + K_2CrO_4 \leftrightarrows 2K(CO_2CH_3) + PbCrO_4 \downarrow.$$

The part precipitated on the outside of the goods can be, and is, at once washed off by rubbing in water, but the particles inside the fibers can come out only by being dissolved, and they are insoluble in water. **Indigo** $C_{16}H_{10}N_2O_2$, which is used in larger amounts than any other dye, belongs to this class. Obtained in early times from several plants in Europe and Egypt, where it was known as woad, and more recently imported from India, where the cultivation of the indigo plant was as important an industry as is the growing of cotton in the Southern States, it is now almost all made artificially. Synthetic indigo is manufactured, with naphthalene $C_{10}H_8$ (p. 411), obtained from gas tar and the tar from by-product coke ovens, as the initial substance. The cloth is saturated with an alkaline solution of indigo white $C_{16}H_{12}N_2O_2$, a soluble, slightly acid substance, and the oxygen of the air subsequently oxidizes this and deposits the insoluble indigo blue within the fibers:

$$2C_{16}H_{12}N_2O_2 + O_2 \rightarrow 2C_{16}H_{10}N_2O_2 \downarrow + 2H_2O.$$

Indanthrene blue is applied in the same way as indigo, and is even less affected by light.

2. **Mordant or Adjective Dyes.** Since cotton is inactive chemically and, although a colloid, has but a slight tendency to adsorb dyes, it is usually necessary first to introduce into the fibers of cotton some colloidal substance with greater adsorptive powers. Substances of this kind are tannic acid for basic dyes, and gelati-

nous colloidal hydroxides, such as those of aluminium, tin, iron and chromium, for non-basic (including acid) dyes. They are called **mordants** (Lat. *mordere*, to bite). Thus, if in three jars we place very dilute solutions of aluminium sulphate, ferric chloride $FeCl_3$ and chromous acetate $Cr(CO_2CH_3)_2$, then add a few drops of a solution of a dye to each, and finally introduce a little of a base (like sodium hydroxide) to precipitate the hydroxide of the metal, this hydroxide will adsorb the dye and carry it into the precipitate. Such a precipitate of mordant and dye is called a **lake**. With the same dye, the three lakes have *different colors*. Thus, in the above-mentioned experiment, if alizarin (madder) is used as the dye, the colors are red (Turkey red), violet, and maroon, respectively. This, of course, is due to the different degrees of dispersion in the three colloidal materials. If aluminium hydroxide is to be used, by first saturating the cloth with hot aluminium acetate solution (p. 560), or by using first aluminium sulphate and then ammonium hydroxide, the aluminium hydroxide is precipitated within the fibers of the goods. When the material is then dyed, the coloring matter is adsorbed by the mordant, with which it forms an insoluble lake, within the fibers. Basic dyes, like Malachite green and Methylene blue, behave similarly with tannic acid, or an insoluble salt of tannic acid, as mordant. It will be seen that, so far as the fabric is concerned, this process, like the first, is a mechanical one, and is independent of the chemical nature of the goods.

3. **Direct or Substantive Dyes.** Most organic dyes are direct dyes on silk or wool, and require no mordant with these materials. The actions seem to be sometimes chemical, but more often cases of adsorption by the silk or wool (both colloids) themselves. A few dyes are also fast on cotton. Congo-red $Na_2C_{32}H_{22}N_6S_2O_6$ is fast both on cotton and wool, but is no longer much used. Chrysophenin is now one of the commonest dyes of this class. These dyes, which are sodium salts of complex organic acids, are colloids like soap (p. 417), and are salted out *within* the fibers of the goods by adding sodium sulphate to coagulate them and assist the adsorption by the cotton. Once adsorbed in this way, unlike soap, they cannot be washed out.

Analytical Reactions of Aluminium Compounds. — The alkalies, and alkaline solutions like that of ammonium sulphide, precipitate the white hydroxide. The product is soluble in excess of the active alkalies. Soluble carbonates also throw down the hydroxide. Aluminium compounds, when heated strongly in the flame with cobalt salts, give a blue aluminate of cobalt $Co(AlO_2)_2$.

Exercises. — 1. What are the differences between zinc and aluminium, and their corresponding compounds?

2. Construct equations showing, (*a*) the hydrolysis of aluminium sulphate (p. 558), (*b*) the interaction of aluminium sulphate and cobalt nitrate in the Bunsen flame.

3. Formulate the ionization of aluminium hydroxide (pp. 557, 531).

4. Why does zinc hydroxide, in spite of its feebleness as a base, dissolve in ammonium hydroxide, while aluminium hydroxide does not?

CHAPTER XLI

GERMANIUM, TIN, LEAD

THE metallic elements of the fifth column of the periodic table are **germanium** (Ge, at. wt. 72.5), **tin** (Sn, at. wt. 119), and **lead** (Pb, at. wt. 207.2). These are on the right side, while **titanium** (Ti, at. wt. 48.1), **zirconium** (Zr, at. wt. 90.6), **cerium** (Ce, at. wt. 140.25), and **thorium** (Th, at. wt. 232.4) occupy the left side.

The Chemical Relations of the Family. — All of these elements show a maximum valence of four. Germanium, tin, and lead are also bivalent. In this respect they resemble carbon and differ from silicon, which is more closely allied to the elements on the left side of the column. The oxides and hydroxides in which these three elements are bivalent become more basic, and the elements themselves more metallic in chemical relations, with increase in atomic weight. In this they resemble the potassium, calcium, and gallium families. Curiously enough, the same three hydroxides are also acidic. They are more strongly acidic than is zinc hydroxide, for the salts they form by interaction with bases are less hydrolyzed than are the zincates. This acidic character likewise increases in the order in which the elements are named above.

GERMANIUM

Germanium (p. 301) forms two oxides GeO and GeO_2 corresponding to those of carbon and of tin. **Germanious oxide** is not very definitely basic or acidic, and the sulphide is the only other well-defined compound of this set. **Germanic oxide** and hydroxide are acidic entirely. The resemblance to carbon is shown in the formation of an unstable compound with hydrogen, of **germanium chloroform** $GeHCl_3$ and of a volatile **chloride** $GeCl_4$ (b.-p. 87°).

TIN

The Chemical Relations of the Element. — Tin is both bivalent and quadrivalent. Each of the oxides and hydroxides SnO and $Sn(OH)_2$, SnO_2 and $SnO(OH)_2$ (or $Sn(OH)_4$), is both basic and acidic, so that there are really four series of compounds. Still, stannous hydroxide is mainly a base, of a feeble sort, while stannic hydroxide is mainly an acid. Thus we have stannous chloride, sulphate, and nitrate, which are stable, although they are all more or less hydrolyzed by water, and sodium stannite $Na_2.SnO_2$ which is unstable. On the other hand, stannic nitrate, sulphate, and chloride are completely hydrolyzed by water, while sodium stannate Na_2SnO_3 is comparatively stable. The dioxide SnO_2 is an infusible solid, resembling silicon dioxide. Tin has a tendency to give complex acids and salts, like H_2SnCl_6, $(NH_4)_2.SnCl_6$, but these are ionized also to a small extent after the manner of double salts, giving ions of Sn^{++++}. Tin forms no salts with weak acids, like carbonic acid.

Occurrence and Extraction. — Tin has long been in use, specimens of it being found in Egyptian tombs. The chief ore of tin is tinstone, or cassiterite SnO_2, which forms square-prismatic crystals whose dark color is due to the presence of iron compounds. The ore is roughly pulverized and washed, to remove granite or slate with which it is mixed, and is then roasted, to oxidize the sulphides of iron and copper, and drive off the arsenic which it contains. After renewed washing to eliminate sulphate of copper and oxide of iron, it is reduced with coal in a reverberatory furnace. The tin is afterwards remelted at a gentle heat, and the pure metal flows away from compounds of iron and arsenic. The metal is produced mainly in Banca and other parts of the East Indies, in Bolivia, and in Cornwall.

Physical and Chemical Properties. — Tin is a silver-white, crystalline metal of low tenacity but great malleability (tin-foil). Its specific gravity is 7.3, and its melting-point about 232°.

Tin is dimorphous (p. 266). In 1851, the tin pipes of an organ were found to have turned largely into a gray powder. In 1868 a shipment of blocks of tin stored in the custom house in Petrograd was found to have changed in the same way. Objects of tin in museums frequently show spots indicating the presence of the "tin pest," as it was called. It now appears that white, metallic tin is stable only above 18°, and that below this temperature it is unstable and is liable to change into gray tin. This transition point is similar to that of sulphur at 96° (p. 265). By immersing the tin in a solution of pink-salt (see below), the change is hastened. When the two kinds of tin are used as the poles of a cell, and are surrounded by pink-salt solution, no difference in potential is observed at 18°. But below 18°, white tin, being unstable, is more active and becomes negative (giving positive ions), while above 18°, gray tin becomes negative.

Tin-plate is made by dipping carefully cleaned sheets of mild steel into molten tin. Vessels of copper are also coated, internally, with tin, to prevent the formation of the basic carbonate (p. 503). For this purpose they are cleaned with ammonium chloride, sprinkled with rosin (to reduce the oxide), and heated to 230°. Molten tin is then spread on the surface with a piece of tow. Alloys of tin, such as bronze (p. 503), soft solder (50 per cent lead), pewter (25 per cent lead), and britannia metal (10 per cent antimony and some copper), are much used in the arts. On account of the action of soft water containing dissolved oxygen on lead (see p. 574), tin pipes are preferred for distributing distilled water and for beer pumps.

Much tin is now recovered by treating old "tin cans" and scrap tin-plate with dry chlorine. The dried gas converts the tin into stannic chloride $SnCl_4$, which is used to make mordants, but hardly attacks the iron (p. 160). The process is called detinning.

Tin, although it displaces hydrogen from dilute acids, is not tarnished by moist air. With warm hydrochloric acid it gives stannous chloride $SnCl_2$ and hydrogen. Hot, concentrated sulphuric acid forms stannous sulphate $SnSO_4$ and sulphur dioxide (*cf.* p. 276). Nitric acid, when cold and dilute, interacts with it, giving stannous nitrate $Sn(NO_3)_2$, and a portion of the nitric acid is reduced to ammonia (*cf.* p. 354). With concentrated nitric acid, stannic nitrate is formed, but most of this salt is hydrolyzed by the water at the high temperature of the action (*cf.* p. 535), and metastannic acid $(H_2SnO_3)_5$ (β-stannic acid) remains. The final result is shown by the equation (simplified):

$$Sn + 4HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O.$$

Tin also displaces hydrogen from caustic alkalies, giving a metastannate, such as sodium metastannate Na_2SnO_3.

Chlorides of Tin. — **Stannous chloride** $SnCl_2,2H_2O$ is made by the interaction of tin and hydrochloric acid. When the crystals are heated, or when a strong aqueous solution is diluted, the salt is partially hydrolyzed. In the latter case the basic chloride $Sn(OH)Cl$ is deposited. By presence of excess of hydrochloric acid, the hydrolysis is prevented. The solution is used as a mordant (p. 565).

Stannous chloride tends to pass into stannic chloride $SnCl_4$, and is therefore an active reducing agent. Thus, it reduces the chlorides of mercury (p. 534) and of the noble metals, liberating the free metals. The action is of the form $Hg^{++} + Sn^{++} \rightarrow Hg + Sn^{++++}$. It also reduces free oxygen, or, what is the same thing, is oxidized by the air. In this case, stannic chloride is formed in the acid solution and the liquid remains clear; in the neutral solution a precipitate of the basic chloride is formed as well:

$$6SnCl_2 + 2H_2O + O_2 \rightarrow 4Sn(OH)Cl + 2SnCl_4.$$

Powdered tin, if placed with the acid solution, will undo the effects of this action by reducing the stannic salt to the stannous condition.

When chlorine acts upon tin, or upon stannous chloride (either solid or dissolved), **stannic chloride** $SnCl_4$ is formed. The compound is a colorless liquid (b.-p. 114°) which fumes very strongly in moist air, giving hydrochloric acid and stannic acid. It is almost completely hydrolyzed by water. The stannic acid which is formed is not precipitated, however, but remains in colloidal suspension:

$$SnCl_4 + 4H_2O \rightleftarrows 4HCl + Sn(OH)_4.$$

The chloride, with small amounts of water, gives hydrates, of which $SnCl_4,5H_2O$, "oxymuriate of tin," is used as a mordant. Double (or perhaps complex) salts, such as ammonium-stannic chloride or "pink-salt" $(NH_4)_2SnCl_6$ (used as a mordant on cotton), are readily formed.

Stannic bromide $SnBr_4$ (b.-p. 201°) resembles stannic chloride.

α-Stannic Acid and its Salts. — When a solution of stannic chloride is treated with ammonium hydroxide, a white, gelatinous precipitate of α-stannic acid is formed:

$$SnCl_4 + 4NH_4OH \rightarrow 4NH_4Cl + H_2SnO_3 + H_2O.$$

The precipitate loses water gradually until the dioxide remains, and neither $Sn(OH)_4$ nor $SnO(OH)_2$ is obtainable as a definite compound. When stannic oxide is fused with caustic soda, **sodium metastannate,** or **α-stannate** $Na_2SnO_3,3H_2O$, is formed:

$$SnO_2 + 2NaOH \rightarrow Na_2SnO_3 + H_2O.$$

This compound is used as a mordant under the name of "preparing salt." When its solution is acidified, α-stannic acid, the actual mordant, is formed by double decomposition. This α-stannic acid interacts readily with acids and alkalies, and the chloride obtained from it is identical with stannic chloride described above.

Flannelette and other cotton goods are rendered non-inflammable by saturation first with sodium α-stannate solution and then, after drying, with ammonium sulphate. The acid is too feeble to form an ammonium salt:

$$Na_2SnO_3 + (NH_4)_2SO_4 \rightarrow Na_2SO_4 + SnO(OH)_2 + 2NH_3.$$

The sodium sulphate is washed out and the goods, after being dried, contain stannic oxide. The latter cannot afterwards be removed by washing, and the material is permanently fireproof. Silk is also loaded with stannic oxide, the amount used varying from 25 to 300 per cent or more.

The α-stannates of the metals, aside from those of potassium and sodium, like the silicates and carbonates which they much resemble, are all insoluble in water, and may be made by double decomposition.

β-Stannic Acid, or Metastannic Acid. — The product of the action of nitric acid upon tin (p. 569) is a hydrated stannic oxide like the foregoing substance, but is not identical with it. It is not easily acted upon by alkalies. By boiling it with caustic soda, however, and then extracting with pure water, a soluble **sodium β-stannate** $Na_2Sn_5O_{11}$ is obtained. β-stannic acid is also very slowly attacked by acids, and the chloride secured from it is not identical with the ordinary chloride. For these reasons it is supposed to be a hydrate of a polymer of stannic oxide $(SnO_2)_5,xH_2O$. When *fused* with caustic soda, it gives the same α-stannate as does the dioxide itself.

The Oxides of Tin. — When stannous oxalate is heated in absence of air, **stannous oxide** SnO remains: $SnC_2O_4 \rightarrow SnO + CO_2 + CO$. It is a black powder which burns in the air, giving the dioxide. The corresponding **hydroxide** $Sn_2O(OH)_2$ is formed by adding sodium carbonate to stannous chloride solution. It is a white powder, easily dehydrated, and interacts with alkalies to give soluble stannites, such as Na_2SnO_2. With acids, the hydroxide gives stannous salts.

Stannic oxide SnO_2 is found in nature (p. 568), and may be made in pure form by igniting β-stannic acid. When heated, it becomes yellow, but recovers its whiteness when cooled (*cf.* Zinc oxide, p. 528). Prepared at a low temperature, it interacts easily with acids, but after strong ignition, is affected by them very slowly.

The Sulphides of Tin. — **Stannous sulphide** SnS is obtained as a dark-brown precipitate when hydrogen sulphide is led into a solution of a stannous salt.

Stannic sulphide SnS_2 is formed likewise by precipitation, and is yellow in color. Stannic sulphide loses sulphur when strongly heated, and leaves stannous sulphide. It is not much affected by dilute acids, but interacts with solutions of ammonium sulphide (or sodium sulphide), giving a soluble **complex sulphide,** namely, **ammonium sulphostannate:**

$$SnS_2 + (NH_4)_2S \rightarrow (NH_4)_2.SnS_3.$$

The corresponding **sodium sulphostannate** is easily crystallized in the form $Na_2SnS_3,2H_2O$. Stannous sulphide is not affected by soluble sulphides, but polysulphides, such as yellow ammonium sulphide, give with it the above-mentioned sulphostannates:

$$SnS + (NH_4)_2S_2 \rightarrow (NH_4)_2.SnS_3.$$

With acids the sulphostannates undergo double decomposition, but the free acid $H_2.SnS_3$ thus produced is unstable and breaks up, giving off hydrogen sulphide, and depositing stannic sulphide.

Analytical Reactions of Salts of Tin. — The two ionic forms of tin, Sn^{++} and Sn^{++++}, are both colorless. Their behavior is different. They give a brown and a yellow sulphide, respectively, with hydrogen sulphide. These sulphides interact with yellow ammonium sulphide (above). The reducing power of stannous-ion Sn^{++} is very characteristic (p. 570). The oxides are reduced by charcoal in the reducing part of the Bunsen flame and the metal is liberated.

LEAD

The Chemical Relations of the Element. — Lead is both bivalent and quadrivalent. The oxides PbO and PbO_2, and the corresponding hydrated oxides, are all both basic and acidic. Lead monoxide is a fairly active base, comparable with cupric oxide, but lead dioxide is a feeble one. Both are feebly acidic. The salts of bivalent lead, like $Pb(NO_3)_2$, commonly called the plumbic salts, are somewhat hydrolyzed by water, but less so than are those of tin. The tetrachloride and other salts of quadrivalent lead are completely hydrolyzed. The plumbites $Na_2.PbO_2$ and plumbates $Na_2.PbO_3$, like the stannites and stannates, are hydrolyzed to a considerable extent. All the compounds in which lead is quadrivalent give up half of the negative radical readily, and are reduced to the "plumbic" condition. The metal displaces hydrogen with difficulty, and is easily displaced by zinc. Lead compounds are all poisonous, and the effects of repeated, very minute doses are cumulative, — resulting in "lead colic." For this reason, the manufacture of white lead is forbidden by law in France, and is subject to strict regulation in other countries.

Occurrence and Metallurgy. — Commercial lead is almost all obtained from galena PbS, which crystallizes in cubes, and is found in the United States (one-third of the world's supply), Spain, and Mexico. This ore often contains considerable amounts of silver sulphide Ag_2S (*cf.* p. 513).

The sulphide of lead is first roasted until a sufficient proportion of it has been converted into the oxide and sulphate. The furnace-doors are then closed, and the temperature raised in order that these products may interact with the unchanged part of the sulphide:

$$PbS + 2PbO \rightarrow 3Pb + SO_2,$$
$$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2.$$

Another plan consists in heating galenite with scrap iron or iron ores and coal: $PbS + Fe \rightarrow Pb + FeS$. The molten ferrous sulphide rises to the top as a matte.

Lead is refined electrolytically by the Betts process. Heavy plates of the crude lead form the anodes, thin sheets of pure lead the cathodes, and a solution of lead fluosilicate $PbSiF_6$ the cell liquid. The operation is similar to that for refining copper (p. 511). Silver, gold and bismuth are left as a sludge.

Physical and Chemical Properties. — Metallic lead is gray in color, very soft, and of small tensile strength. Its specific gravity is 11.4, and its melting-point 327.4°. While warm, it is formed by hydraulic pressure into pipes which are used in plumbing and for covering electric cables. On account of its very slow interaction with most substances, sheet lead is used in chemical factories, for example, to line sulphuric-acid chambers. An alloy containing 0.5 per cent of arsenic is used in making small shot and shrapnel bullets. Type-metal contains 20–25 per cent of antimony and expands on solidifying, giving a perfect reproduction of the mold. In both cases greater hardness is secured by the addition of the foreign metal. Solder contains 50 per cent of tin and, being a solution, melts at a low temperature.

Lead oxidizes very superficially in the air. The suboxide Pb_2O is supposed to be first formed. The final covering is a basic carbonate. Contact with hard waters confers upon lead a similar coating composed of the carbonate and the sulphate. These deposits, being insoluble and strongly adherent, enclose the metal and protect the water from contamination with lead compounds. Pure rain-water, however, since it has no hardness, and contains oxygen in solution, gives the hydroxide $Pb(OH)_2$, which is noticeably soluble. Hence lead pipes can safely be used only with somewhat hard water. When heated in the air, lead gives the monoxide PbO or minium Pb_3O_4, the latter at lower temperatures.

The metal displaces hydrogen from hydrochloric acid slowly. It is hardly affected by cold concentrated sulphuric acid (*cf.* p. 284). Nitric acid attacks it readily, giving lead nitrate and oxides of nitrogen (p. 354).

Chlorides and Iodide. — **Plumbic chloride** $PbCl_2$ is precipitated when a soluble chloride is added to a solution of a lead salt. It is slightly soluble in water (1.5 : 100) at 18°, and much more so at 100°.

Lead tetrachloride $PbCl_4$ is a solid at −15°, and loses chlorine at the ordinary temperature. It is made by passing chlorine into plumbic chloride suspended in hydrochloric acid. The solution contains H_2PbCl_6. Ammonium chloride is added and ammonium chloroplumbate $(NH_4)_2PbCl_6$ crystallizes out. When this is thrown into cold, concentrated sulphuric acid, an oil, $PbCl_4$, settles to the bottom. The oil fumes in the air, and closely resembles stannic chloride $SnCl_4$. With little water, it slowly deposits $PbCl_2$ and gives off chlorine. With much water it is quickly hydrolyzed, and lead dioxide is thrown down:

$$PbCl_4 + 2H_2O \rightarrow PbO_2 + 4HCl.$$

The yellow **lead iodide** PbI_2 is formed by precipitation. It crystallizes in yellow scales from solution in hot water.

Oxides and Hydroxides. — There are five different oxides of lead, Pb_2O, PbO, Pb_3O_4, Pb_2O_3, and PbO_2. The **suboxide** Pb_2O is a dark-gray powder, formed by gently heating the oxalate. **Plumbic oxide,** or lead monoxide PbO, is made by cupellation (p. 513) of lead, and the solidified, crystalline mass of yellowish-red color is sold as **litharge.** All the other oxides yield this one when they are heated above 600° in the air. Plumbic oxide takes up carbon dioxide from the air, and therefore usually contains a basic carbonate. The oxide is used in making glass and enamels and for preparing salts of lead. Mixed with glycerine, it gives a cement for glass or stone.

Plumbic hydroxide $Pb(OH)_2$ is formed by precipitation. It gives up water in stages, the successive products being $Pb(OH)_2$, $Pb_2O(OH)_2$, $Pb_3O_2(OH)_2$. These substances are equivalent in composition to PbO,H_2O, $2PbO,H_2O$, and $3PbO,H_2O$ respectively. The hydroxide is observably soluble in water, and gives a solution with a faintly alkaline reaction. With acids it forms salts of lead. It interacts also with potassium and sodium hydroxides to form the soluble **plumbites,** like **sodium plumbite** $Na_2.PbO_2$.

Minium, or **red lead,** Pb_3O_4, gives off oxygen when heated:

$$2Pb_3O_4 \rightleftarrows 6PbO + O_2.$$

On account of unequal heating during manufacture, commercial red lead is never fully oxidized, and always contains litharge. Conversely, commercial litharge usually contains a little minium.

Minium, when heated with warm, dilute nitric acid, is decomposed, and leaves lead dioxide as an insoluble powder. Two-thirds of the lead is basic and one-third is acidic. Minium is therefore lead orthoplumbate (see below):

$$Pb_2.PbO_4 + 4HNO_3 \rightleftarrows 2Pb(NO_3)_2 + H_4PbO_4.$$

The double decomposition as a salt that it thus undergoes is followed by dehydration of the plumbic acid, which is unstable ($H_4PbO_4 \rightarrow PbO_2 + 2H_2O$), and the dioxide remains. Red lead is used in glass-making, and, when mixed with oil, gives a red paint.

Lead dioxide PbO_2 may be obtained as described above in the form of a brown powder. It is usually made by adding bleaching powder to an alkaline solution of plumbic hydroxide:

$$Na_2.PbO_2 + Ca(OCl)Cl + H_2O \rightarrow 2NaOH + CaCl_2 + PbO_2\downarrow.$$

In this action we may regard the free lead hydroxide, formed by hydrolysis of the plumbite, as being oxidized by the bleaching powder. Lead dioxide is an active oxidizing agent. It interacts with, and sets fire to, a stream of hydrogen sulphide, and it liberates chlorine from hydrochloric acid. With acids it gives no hydrogen peroxide, and is not a peroxide (peroxidate) in the restricted sense of the term (p. 223). Lead dioxide interacts with potassium and sodium hydroxides, giving soluble **plumbates.** The potassium salt $K_2PbO_3,3H_2O$ is analogous to the metastannate $K_2SnO_3,3H_2O$ (p. 571). A mixture of calcium carbonate and lead monoxide absorbs oxygen when heated in a stream of air, and the yellowish-red calcium orthoplumbate is formed:

$$4CaCO_3 + 2PbO + O_2 \rightleftarrows 2Ca_2PbO_4 + 4CO_2.$$

The action is reversible, and is at the basis of Kassner's method of manufacturing oxygen from the air.

Other Salts of Lead. — **Lead nitrate** $Pb(NO_3)_2$ may be made by treating lead, lead monoxide, or lead carbonate with nitric acid. It forms white, anhydrous octahedra. The nitrate and acetate (see below) are the salts of lead which, because of their solubility (see Table), are most commonly used. On account of hydrolysis, the solution of the nitrate is acid in reaction.

Lead carbonate $PbCO_3$ is found in nature. It may be formed as a precipitate by adding sodium bicarbonate to lead nitrate solution.

With normal sodium carbonate, a basic carbonate $Pb_3(OH)_2(CO_3)_2$ is deposited. This basic salt is identical with **white lead,** which on account of its superior opacity, has better covering power than zinc-white (p. 528) or permanent white (p. 496). The substance is manufactured in various ways, all of which involve the oxidation of the lead by the air, the formation of a basic acetate by the interaction of vinegar or acetic acid with the oxide, and the subsequent decomposition of the salt by carbon dioxide. The best quality is obtained by the Dutch method. In this, gratings of cast lead ("buckles") are placed above a shallow layer of vinegar in small pots. These pots are buried in manure, which by its decomposition furnishes the carbon dioxide and the necessary warmth. The gratings are gradually converted into a white mass of the basic carbonate. The vapor of acetic acid arising from the vinegar may be regarded as a catalytic agent, since it is used over and over again.

Lead acetate $Pb(C_2H_3O_2)_2,3H_2O$ is made by the action of acetic acid on litharge. It is easily soluble in water and, from the sweet taste of the solution, is named **sugar of lead** (used in medicine). The basic salt $Pb(OH)(C_2H_3O_2)$ is formed by boiling a solution of lead acetate with excess of litharge. Unlike most basic salts, this basic salt is soluble in water, and its solution has a faintly alkaline reaction.

Lead sulphate $PbSO_4$ occurs in nature as anglesite. Being insoluble in water, it is easily obtained by precipitation.

Natural **lead sulphide** PbS (galena) forms black, cubic crystals with a silvery luster. The precipitated salt is amorphous. It is more easily attacked by active acids than is mercuric sulphide (*cf.* p. 531).

The Storage Battery.—In the ordinary **lead accumulator** the plates consist of leaden gratings. The openings are filled with finely divided lead in one plate and with lead dioxide in the other. These, and the dilute sulphuric acid in the cell, are the active substances when the cell is charged. When the battery is used, the $SO_4^=$ ions migrate towards the plates filled with the lead (Fig. 131), and convert this into a mass of the insoluble lead sulphate: $SO_4^= + Pb \rightarrow PbSO_4 + 2\ominus$. These plates receive the negative charges. Simultaneously, the H^+ ions move towards the other plates and there reduce to monoxide the lead dioxide with which they are filled.

$$PbO_2 + 2H^+ \rightarrow H_2O + PbO + 2\oplus.$$

These plates acquire positive charges and, by interaction of the lead monoxide with the sulphuric acid, become filled, like the negative plates, with lead sulphate. During the discharge, much sulphuric acid is thus removed from the cell fluid, and the approaching exhaustion of the cells can thus be ascertained by measuring the specific gravity of the fluid. The E.M.F. of the current is a little over 2 volts.

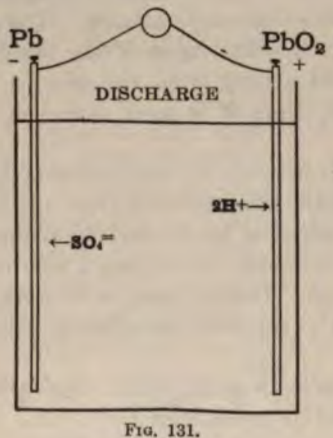


FIG. 131.

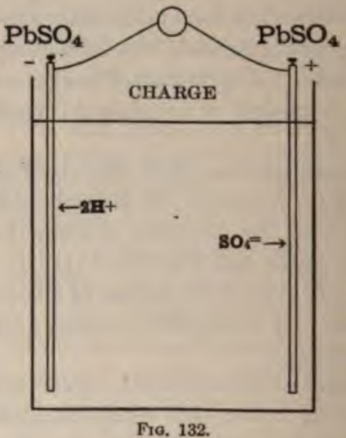


FIG. 132.

The charging is done by passing a current through the cell, in the opposite direction to the one which it yields (Fig. 132). The H^+ ions are attracted to the negative plate and an equivalent number of $SO_4^=$ ions are formed, so that only lead remains:

$$PbSO_4 + 2H^+ + 2\ominus \rightarrow Pb + 2H^+ + SO_4^=.$$

Simultaneously, the $SO_4^=$ is attracted by the positive plate and, with the lead sulphate there present, forms lead persulphate: $SO_4^= + PbSO_4 + 2\oplus \rightarrow Pb(SO_4)_2$. The persulphate, being a salt of quadrivalent lead, is at once hydrolyzed and the filling of this plate is thus changed into lead dioxide: $Pb(SO_4)_2 + 2H_2O \rightarrow PbO_2 + 2H_2SO_4$. Both plates are thus brought back to the condition in which they were before the discharge.

The last set of charges consumes energy, while the first set liberates energy. Both may be stated in a single equation:

$$2PbSO_4 + 2H_2O \underset{\leftarrow \text{discharge}}{\overset{\text{charge} \rightarrow}{\rightleftarrows}} Pb + 2H_2SO_4 + PbO_2.$$

In the **Edison cell,** when charged, one plate is of iron and the other contains nickelic oxide Ni_2O_3. The cell liquid is a solution of potassium hydroxide. When the cell operates, the nickelic oxide is reduced to $Ni(OH)_2$ and the iron is oxidized to $Fe(OH)_2$, an action which delivers energy:

$$Fe + 3H_2O + Ni_2O_3 \rightleftarrows Fe(OH)_2 + 2Ni(OH)_2.$$

When the cell is charged, the nickel is reoxidized and the iron reduced.

Paints. — A paint usually contains three ingredients:

1. *The oil* hardens to a tough resin on exposure to the air ("dries") and adheres firmly to the surface being painted.
2. *The body* is a fine powder which makes the paint opaque. Since the powder does not shrink, it also "fills" the paint and prevents the formation of minute pores which otherwise would appear in the oil after drying. White lead (p. 577) is a common material for the body, but zinc oxide, lithopone (p. 497) and other substances are used.
3. Except in the case of white paint, *a pigment* is added. Various oxides, such as minium, colored salts, and lakes (p. 565) are used as coloring matters.

The oil does not "dry" by evaporation but gives a resin by oxidation. Linseed oil and hemp oil are commonly used. They contain glyceryl esters (p. 414) of *unsaturated* acids, such as that of linoleic acid $C_3H_5(CO_2C_{17}H_{31})_3$, which contains four units of hydrogen less than stearic acid. The unsaturated part of the molecule takes up the oxygen. By previously boiling the oil with manganese dioxide and other oxides, it is rendered more active, and "dries" more quickly.

Plumbers use a cement made of minium and linseed oil, in which the former oxidizes the latter, without access of air being necessary.

Analytical Reactions of Lead Compounds. — Hydrogen sulphide precipitates the black sulphide, even when dilute acids are present. Sulphuric acid throws down the sulphate. Potassium hydroxide gives the white hydroxide, which dissolves in excess to form the plumbite. Potassium chromate or dichromate (*q.v.*) gives a yellow precipitate of **lead chromate** $PbCrO_4$, which is used as a pigment under the name of "chrome-yellow."

TITANIUM, ZIRCONIUM, CERIUM, THORIUM

The metals on the left side of the fifth column of the periodic table are all quadrivalent, although compounds in which a lower valence appears are numerous in this family. The first two are feebly base-forming as well as feebly acid-forming; the last two are base-forming exclusively.

Titanium occurs in rutile $TiTiO_4$. Derived from it are a number of titanates of the form K_2TiO_3. **Zirconium** is found in zircon, the orthosilicate of zirconium $ZrSiO_4$. The oxide is used in making the incandescent substance in some forms of gas lamps.

Cerium occurs chiefly in cerite [Ce, La, Nd, Pr] SiO_4,H_2O (*cf.* p. 443). The particles of an alloy of cerium (70 per cent) and iron (30 per cent), when torn off by a file, catch fire in the air. This fact is utilized in making **gas-lighters** and cigar-lighters. **Thorium** is found in thorite $ThSiO_4$, but most of the supply comes from monazite sand. The nitrate $Th(NO_3)_4,6H_2O$ is used in making Welsbach incandescent mantles (*cf.* Flame, p. 397). The compounds are radioactive (see Radium).

The foundation of the **Welsbach mantle** is woven of ramie. This is saturated with a solution of thorium and cerium nitrates in the proportion 99 : 1, and is then molded to the proper shape and dried. By heating in a Bunsen flame, the organic matter is burned, and the nitrates are decomposed:

$$Th(NO_3)_4 \rightarrow ThO_2 + 4\,NO_2 + O_2.$$

The oxides retain the form of the fabric and, to prevent breakage in handling, the structure is dipped in collodion and dried.

Exercises. — 1. In what order should you place the elements dealt with in this chapter, beginning with the least metallic, and ending with the most metallic (p. 436)?

2. Construct equations showing, (*a*) the interaction of tin and concentrated sulphuric acid, (*b*) of water and stannous chloride, (*c*) of oxygen and stannous chloride in acid solution, (*d*) the decomposition of lead oxalate (p. 575), (*e*) the interaction of lead monoxide and acetic acid, (*f*) and of lead monoxide and lead acetate.

3. To which class of ionic actions (pp. 259, 270, 504) do the reductions by stannous chloride and by tin (p. 570) belong?

4. What interactions probably occur when lead dioxide liberates chlorine from hydrochloric acid?

5. How should you set about preparing, (*a*) lead oxalate (insoluble), (*b*) lead chlorate (soluble)?

6. Construct equations for the formation of white lead by the Dutch process, showing, (1) the formation of the basic acetate by the action of oxygen, water, and acetic acid vapor, and (2) the action of carbonic acid on the product.

CHAPTER XLII

ARSENIC, ANTIMONY, BISMUTH

THIS family is very closely related to the elements phosphorus and nitrogen which precede it in the same column of the periodic table. In reading this chapter, therefore, constant reference should be made to the chemistry of the corresponding compounds of phosphorus. For a general comparison of the elements **arsenic** (As, at. wt. 75), **antimony** (Sb, at. wt. 120.2) and **bismuth** (Bi, at. wt. 208) with each other and with the two already disposed of, see p. 592. It is sufficient here to say that arsenic is mainly an acid-forming element, and is therefore a non-metal, while antimony is both acid-forming and base-forming, and bismuth is base-forming. Each of the three elements gives two sets of compounds, in which it is trivalent, and quinquivalent, respectively. None of the elements when free displaces hydrogen from dilute acids.

ARSENIC As

The Chemical Relations of the Element. — Arsenic forms a compound with hydrogen AsH_3. It gives several halogen derivatives of the type AsX_3, which are completely hydrolyzed by water. Its oxides and hydroxides are acidic.

Sulphates, nitrates, carbonates, and other salts of arsenic are not formed. The complex sulphides (p. 572) are important.

Occurrence and Preparation. — Arsenic is found free in nature. It occurs also in combination with many metals, particularly in arsenical pyrites (mispickel) FeAsS. Two sulphides of arsenic, orpiment As_2S_3 and realgar As_2S_2, and an oxide As_2O_3, are less common.

The element is obtained either from the native material or by heating arsenical pyrites: $FeAsS \rightarrow FeS + As$. During the roasting of the sulphur ores of metals, arsenic trioxide is formed by the oxidation of the arsenic so frequently present, and collects as a dust in the flues. The supply is greatly in excess of the demand.

Physical and Chemical Properties. — The free element is steel-gray in color, metallic in appearance, and crystalline in form. It gives off vapor at 180°, and above 600° acquires a vapor pressure of 760 mm. The density of the vapor measured at 644° gives 308.4 as the weight of the G.M.V. (22.4 liters at 0° and 760 mm.). The weight of arsenic combining with one chemical unit weight (35.46 g.) of chlorine is 25 g. Three times this amount, or 75 g., is the smallest weight found in the G.M.V. of any volatile compound of arsenic, and is therefore accepted as the atomic weight (p. 106). Since 308.4 is equal approximately to 4×75 (= 300), the formula of the vapor of the simple substance at 644° is As_4. At 1700° the formula is As_2 (*cf.* p. 117).

The free element burns in the air, producing clouds of the solid trioxide As_2O_3. It unites directly with the halogens, with sulphur, and with many of the metals. When boiled with nitric acid, chlorine-water, and other powerful oxidizing agents (p. 157), it is oxidized in the same way as is phosphorus, and yields arsenic acid H_3AsO_4.

Arsine AsH_3. — This substance corresponds in composition to ammonia and phosphine, and some of the ways in which it may be formed are analogous to those used in the case of these substances. Thus, when arsenic and zinc are melted together in the proportions to form **zinc arsenide** Zn_3As_2, and the product is treated with dilute hydrochloric acid, the result is similar to the action of water or dilute acids upon calcium phosphide, and arsine is evolved as a gas:

$$Zn_3As_2 + 6HCl \rightarrow 2AsH_3 + 3ZnCl_2.$$

Arsine (arsenuretted hydrogen) is formed also by the action of nascent hydrogen (*cf.* p. 360) upon *soluble* compounds of arsenic. When a solution of arsenious chloride $AsCl_3$ or arsenic acid is added to zinc and hydrochloric acid in a generating flask, arsine is formed:

$$AsCl_3 + 3H_2 \rightarrow AsH_3 + 3HCl.$$

Pure arsine may be secured by leading the mixture with hydrogen through a U-tube immersed in liquid air. The arsine (b.-p. −55°) condenses as a colorless liquid (m.-p. −119°).

Arsine burns with a bluish flame, producing water and clouds of arsenic trioxide: $2AsH_3 + 3O_2 \rightarrow 3H_2O + As_2O_3$. The combustion of hydrogen containing arsine, generated as just described, gives the same substances. Since arsine, when heated, is readily dissociated into its constituents (*cf.* p. 268), the vapor of free arsenic is present in the interior of the hydrogen flame. This arsenic may be condensed in the form of a metallic-looking, brownish stain by interposition of a cold vessel of white porcelain (*cf.* Fig. 85, p. 268). Even when only a trace of the compound of arsenic has been added to the materials in the generator, the stain which is produced is very conspicuous. This behavior thus furnishes us with the basis of an exceedingly delicate test — **Marsh's test** — for the presence of arsenic in any soluble form of combination. The compounds of antimony alone show a similar phenomenon (see Stibine).

Arsine is exceedingly **poisonous**, the breathing of small amounts producing fatal effects. It differs from ammonia more markedly than does phosphine, for it is not only without action on water or acids, but does not unite directly even with the halides of hydrogen.

Halides of Arsenic. — The halides include a liquid **trifluoride** AsF_3, a liquid trichloride, a solid **tribromide** $AsBr_3$, and a solid **tri-iodide** AsI_3.

The **trichloride** $AsCl_3$, which is prepared by passing chlorine gas into a vessel containing arsenic, is easily formed as the result of a vigorous action. It is a colorless liquid (b.-p. 130°). When mixed with water it is at once converted into the white, almost insoluble trioxide. The action is presumably similar to that of water upon the corresponding compound of phosphorus (p. 372), but the arsenious acid for the most part loses water and forms the insoluble anhydride:

$$AsCl_3 + 3H_2O \rightleftarrows As(OH)_3 + 3HCl,$$
$$2As(OH)_3 \rightleftarrows As_2O_3 \downarrow + 3H_2O.$$

This action, however, differs markedly from the other in that it is reversible, and arsenic trioxide interacts with aqueous hydrochloric acid, giving a solution of arsenious chloride. When this solution is boiled, arsenious chloride escapes along with the vapor.

Oxides of Arsenic. — **Arsenic trioxide** As_2O_3 is produced by burning arsenic in the air and during the roasting of arsenical ores (p. 582), and is known as "white arsenic" or simply "arsenic." It is purified for commercial purposes by subliming the flue-dust in cylindrical pots. The pure trioxide is deposited in a glassy form in the upper part of the vessel. Its vapor density shows it to have the formula As_4O_6.

When treated with water, the trioxide goes into solution to slight extent (1.2 : 100 at 2°), forming arsenious acid, by reversal of the second of the actions given above. In boiling water the solubility is greater (11.5 : 100). When heated in a tube with carbon, this oxide is reduced, and the free element, being volatile, is deposited upon the cold part of the tube just above the flame. The trioxide is an active poison, since it gradually passes into solution, forming arsenious acid. The fatal dose is 0.06–0.18 g. (1–3 grains), but "arsenic eaters" become tolerant of it and can take four times as much without evil effects.

The **pentoxide** As_2O_5 is a white crystalline substance, formed by heating arsenic acid: $2H_3AsO_4,H_2O \rightarrow As_2O_5 + 4H_2O$. When raised to a higher temperature, it loses a part of its oxygen, leaving the trioxide. In consequence of this instability, it cannot be formed by direct union of oxygen with the trioxide, after the manner of phosphorus pentoxide.

Acids of Arsenic. — When elementary arsenic or arsenious oxide is treated with concentrated nitric acid, or with chlorine and water, **orthoarsenic acid** H_3AsO_4 is produced. The substance crystallizes as a deliquescent white solid $2H_3AsO_4,H_2O$. *Salts* of this acid, and of pyroarsenic acid $H_4As_2O_7$ and metarsenic acid $HAsO_3$, corresponding to the phosphoric acids (p. 368), are known. The two last acids, themselves, however, are not known as such. It has been shown by Menzies that, when the hemihydrate of orthoarsenic acid is dried at 100°, the only acid obtainable has the composition $H_5As_3O_{10}(= 5H_2O,3As_2O_5)$. When this acid is heated more strongly, it loses water, leaving the pentoxide As_2O_5. With metaphosphoric acid, the final elimination of all the water by simple heating is impossible. The chocolate-brown **silver orthoarsenate** Ag_3AsO_4 and the white $MgNH_4AsO_4$, like the corresponding phosphates, are insoluble in water.

Arsenious acid H_3AsO_3, like sulphurous and carbonic acids, loses water, and yields the anhydride (arsenic trioxide) when the attempt is made to obtain it from the aqueous solution. The **potassium** and **sodium arsenites,** K_3AsO_3 and Na_3AsO_3, are made by treating arsenic trioxide with caustic alkalies, and are much hydrolyzed by water. The arsenites of the heavy metals are insoluble, and can be made by precipitation. Scheele's green is an arsenite of copper $CuHAsO_3$. In cases of poisoning by white arsenic, freshly precipitated ferric hydroxide (or the same compound in colloidal suspension) or magnesium hydroxide is administered, since by interaction with the arsenious acid they form insoluble substances.

Sulphides of Arsenic. — **Arsenic pentasulphide** As_2S_5 is obtained as a yellow powder by decomposition of the sulpharsenates (see below), and by leading hydrogen sulphide into the solution of arsenic acid in concentrated hydrochloric acid which contains $AsCl_5$.

Arsenious sulphide As_2S_3 occurs in nature as orpiment, and was formerly used as a yellow pigment (*auripigmentum*). The word arsenic is derived from the Greek name for this mineral (ἀρσενικόν). It is obtained as a citron-yellow precipitate when hydrogen sulphide is led into an aqueous solution of arsenious chloride.

When hydrogen sulphide is led into an aqueous solution of arsenious acid, the sulphide is formed, but remains in **colloidal suspension.** It is a negatively charged colloid (p. 417), a small amount of H^+ ion in the liquid rendering the whole electrically neutral. It is coagulated by adding solutions of salts, lower concentrations being sufficient the higher the valence of the positive ion of the salt (0.05 Molar KCl, 0.0007 M $BaCl_2$, 0.00009 M $AlCl_3$).

Realgar As_2S_2 is a natural sulphide of orange-red color, and is also manufactured by subliming a mixture of arsenical pyrites and pyrite:

$$2FeAsS + 2FeS_2 \rightarrow 4FeS + As_2S_2\uparrow.$$

It burns in oxygen, forming arsenious oxide and sulphur dioxide, and is mixed with potassium nitrate and sulphur to make "Bengal lights."

Sulpharsenites and Sulpharsenates. — The sulphides of arsenic interact with solutions of alkali sulphides after the manner of the sulphides of tin (p. 572), giving soluble, complex sulphides. Arsenious sulphide with colorless ammonium sulphide gives ammonium sulpharsenite, and with the yellow sulphide gives ammonium sulpharsenate:

$$3(NH_4)_2S + As_2S_3 \rightarrow 2(NH_4)_3.AsS_3,$$
$$3(NH_4)_2S + As_2S_3 + 2S \rightarrow 2(NH_4)_3.AsS_4.$$

Proustite (p. 512) is a natural sulpharsenite of silver.

These salts are decomposed by acids, and give the feebly ionized sulpharsenious or sulpharsenic acid:

$$(NH_4)_3.AsS_3 + 3HCl \rightarrow 3NH_4Cl + H_3AsS_3 \rightarrow 3H_2S\uparrow + As_2S_3\downarrow,$$
$$(NH_4)_3.AsS_4 + 3HCl \rightarrow 3NH_4Cl + H_3AsS_4 \rightarrow 3H_2S\uparrow + As_2S_5\downarrow.$$

These sulpho-acids, however, at once break up, giving hydrogen sulphide as a gas, and the sulphides of arsenic as yellow precipitates.

ANTIMONY Sb

The Chemical Relations of the Element. — Antimony resembles arsenic in forming a hydride SbH_3 and halides of the forms SbX_3 and SbX_5. The latter are partially hydrolyzed by water with ease, but complete hydrolysis is difficult to accomplish with cold water. The oxide Sb_2O_3 is basic and also feebly acidic (amphoteric), and the oxide Sb_2O_5 is acidic. The compositions of the compounds are similar to those of the compounds of arsenic, but there are in addition salts, such as $Sb_2(SO_4)_3$, derived from the oxide Sb_2O_3. The element gives complex sulphides.

Occurrence and Preparation. — Antimony occurs free in nature. The black trisulphide Sb_2S_3, stibnite, is found in Hungary and Japan, and forms shining, prismatic crystals. Stibnite is roasted in the air in order to remove the sulphur, and the white oxide which remains is mixed with carbon and reduced by strong heat:

$$Sb_2S_3 + 5O_2 \rightarrow Sb_2O_4 + 3SO_2,$$
$$Sb_2O_4 + 4C \rightarrow 2Sb + 4CO.$$

Properties. — Antimony is a white, crystalline metal, melting at 630° (b.-p. 1300°). It is brittle, and easily powdered. Its vapor at 1640° has the formula Sb_2, while at lower temperatures Sb_4 is present. It is **used** in making alloys such as type-metal, stereotype-metal, and britannia metal (*q.v.*). The alloys of antimony expand during solidification, and therefore give exceptionally sharp castings.

Babbitt's Metal (Sb 3, Zn 69, As 4, Pb 5, Sn 19), and other **anti-friction alloys** used in lining bearings, contain antimony along with zinc, copper, and other metals. Molten mixtures of metals (alloys), when solidifying, do not always form a homogeneous, solid mass. In an anti-friction alloy, what is wanted is a mass, in general soft, but containing hard particles. The latter bear most of the pressure, yet, as the alloy wears, *they are pressed into the softer matrix* so that a smooth surface is always presented. An alloy which has the opposite composition, that is, which gives a hard mass containing softer particles, develops heat by friction much more rapidly.

The element unites directly with the halogens. It does not rust, but when heated it burns in the air, forming the trioxide Sb_2O_3 or a higher oxide Sb_2O_4. When heated with nitric acid, it yields the trioxide and, with more difficulty, antimonic acid H_3SbO_4.

Stibine SbH_3. — The hydride of antimony SbH_3 is formed by the action of zinc and hydrochloric acid on any soluble compound of antimony. By the action of dilute, cold hydrochloric acid on an alloy of antimony and magnesium (1 : 2), a mixture of hydrogen and stibine containing as much as 11.5 per cent (by volume) of the latter may be made. It is separated by cooling with liquid air (b.-p. −17°, m.-p. −88°). It is more easily dissociated than is arsine (p. 584), and forms a deposit of antimony when a porcelain vessel is held in the flame.

Antimony Halides. — The halides include the trichloride; the **pentachloride** $SbCl_5$, a liquid (m.-p. −6°, b.-p. 140°); the **tribromide** $SbBr_3$, **tri-iodide** SbI_3, **trifluoride** SbF_3, and **pentafluoride** SbF_5.

Antimony trichloride $SbCl_3$ is made by direct union of chlorine and antimony. It forms large, soft crystals (m.-p. 73°, b.-p. 223°), and used to be named "butter of antimony." When treated with little water, it forms a white, opaque, insoluble basic salt, antimony oxychloride:

$$SbCl_3 + H_2O \rightleftarrows SbOCl\downarrow + 2HCl.$$

With a large amount of water, a greater proportion of the chlorine is removed, and $Sb_4O_5Cl_2$ ($= 2SbOCl,Sb_2O_3$) remains. With boiling water the oxide is finally formed. The action is not complete as long as hydrochloric acid is present. It may therefore be reversed, so that, on addition of hydrochloric acid to the mixture, a clear solution of the trichloride is re-formed. If the concentration of the acid is once more reduced by dilution with water, the oxychloride is again precipitated.

Oxides of Antimony. — The **trioxide** Sb_2O_3 (vapor density gives Sb_4O_6) is obtained by oxidizing antimony with nitric acid, or by combustion of antimony with a limited supply of oxygen. It is a white substance, insoluble in water. It is in the main a basic oxide, interacting with many acids to form salts of antimony. But it interacts also with alkalies, giving soluble **antimonites.** The **pentoxide** Sb_2O_5 is a yellow, amorphous substance, obtained by heating antimonic acid. It combines only with bases to form salts, and is therefore an acid-forming oxide exclusively. The **tetroxide** Sb_2O_4 is formed by heating antimony or the trioxide in excess of oxygen. It is neither acid- nor base-forming.

Salts of Antimony. — The **nitrate** $Sb(NO_3)_3$ and the **sulphate** $Sb_2(SO_4)_3$ are made by the interaction of the trioxide with nitric and sulphuric acids. They are hydrolyzed by water, giving basic salts, such as $(SbO)_2SO_4$ ($= Sb_2O_2SO_4$), which, like SbOCl, are derived from the hydroxide SbO(OH). When the trioxide is heated with a solution of potassium bitartrate KHC_4HO_6, a basic salt $K(SbO)C_4H_4O_6,\frac{1}{2}H_2O$, known as **tartar-emetic,** is formed. This is a white, crystalline substance which is soluble in water and is used in medicine. The univalent group SbO^I is known as **antimonyl,** and the above mentioned basic compounds are often called antimonyl sulphate, etc.

Antimonic Acid. — By vigorous oxidation of antimony with nitric acid, or by decomposing the pentachloride with water, a white, insoluble substance of the approximate composition H_3SbO_4 is obtained. This substance interacts with caustic potash and passes into solution. But the salts which have been made are pyro- and metantimoniates. Thus, when antimony is fused with niter, **potassium metantimoniate** $KSbO_3$ is formed. When dissolved, this salt takes up water, giving a solution of the **acid potassium pyroantimoniate:**

$$2KSbO_3 + H_2O \rightarrow K_2H_2Sb_2O_7.$$

If this is added to a strong solution of a salt of sodium, an **acid sodium pyroantimoniate** is thrown down, $Na_2H_2Sb_2O_7$. This is almost the only somewhat insoluble salt of sodium.

Sulphides of Antimony. — The **trisulphide** Sb_2S_3 is found in nature as the black, crystalline stibnite. As precipitated from solutions of salts of antimony, the trisulphide is an orange-red powder, which, however, after being melted, assumes the appearance of stibnite:

$$2SbCl_3 + 3H_2S \rightleftarrows Sb_2S_3 \downarrow + 6HCl.$$

Antimony trisulphide, like cadmium sulphide (p. 531), cannot be precipitated in presence of concentrated hydrochloric acid.

The **pentasulphide** Sb_2S_5 is obtained by the decomposition of the sulphantimoniates (see below). In appearance it resembles the trisulphide and, when heated, decomposes into this substance and free sulphur.

The sulphides of antimony behave towards solutions of the alkali sulphides as do the sulphides of arsenic (p. 587). The trisulphide dissolves in colorless ammonium sulphide with difficulty, forming an unstable, soluble **ammonium sulphantimonite**

$$Sb_2S_3 + 3(NH_4)_2S \rightarrow 2(NH_4)_3SbS_3.$$

With the pentasulphide or with yellow ammonium sulphide the soluble **ammonium sulphantimoniate** is readily formed:

$$Sb_2S_5 + 3(NH_4)_2S \rightarrow 2(NH_4)_3.SbS_4,$$
$$Sb_2S_3 + 3(NH_4)_2S + 2S \rightarrow 2(NH_4)_3.SbS_4.$$

The most familiar substance of this class is **Schlippe's salt** Na_3SbS_4, $9H_2O$. Pyrargyrite (p. 512) is a natural sulphantimonite.

When acids are added to solutions of sulphantimoniates, the sulphantimonic acid which is liberated decomposes, and antimony pentasulphide is thrown down (see under Arsenic, p. 587).

BISMUTH

The Chemical Relations of the Element. — Bismuth forms no compound with hydrogen. Its compounds with the halogens are of the form BiX_3 and are hydrolyzed by water giving basic salts. The oxide Bi_2O_3 is basic, and the oxide Bi_2O_5 is not acidic. Bismuth gives a carbonate, nitrate, phosphate, and other salts, in which it acts as a trivalent element. It forms no soluble complex sulphides.

Occurrence and Properties. — This element is found free in nature, and also as trioxide Bi_2O_3 and trisulphide Bi_2S_3. It is a shining, brittle metal with a reddish tinge (m.-p. 271°). Bismuth is one of the few substances (see water) which expand on solidifying, the crystals being lighter than the liquid at 271°. It is dimorphous, with a transition point (p. 86) at 75°. Mixtures of bismuth with other metals of low melting-point fuse at lower temperatures than do the separate metals. This is a corollary of the fact that a solution freezes at a lower temperature than does the pure solvent (p. 134). Thus, Wood's metal, containing bismuth (m.-p. 271°) 4 parts, lead (m.-p. 327°) 2 parts, tin (m.-p. 232°) 1 part, and cadmium (m.-p. 321°) 1 part, melts at 60.5°, considerably below the boiling-point of water. Similar alloys are used for safety plugs in steam-boilers and automatic sprinklers.

Bismuth does not tarnish, but when heated strongly it burns to form the trioxide. With the halogens it forms a **fluoride** BiF_3, a **bromide** $BiBr_3$, and an **iodide** BiI_3. When the metal is treated with oxygen acids, or the trioxide with any acids, salts are produced.

Compounds of Bismuth. — In addition to the basic **trioxide** Bi_2O_3, which is a yellow powder obtained by direct oxidation of the metal or by ignition of the nitrate, three other oxides are known — BiO, Bi_2O_4, and Bi_2O_5. None of these, however, is either acid-forming or base-forming.

The salts of bismuth, when dissolved in water, give insoluble basic salts, and the actions are reversible, the basic salts being redissolved by addition of an excess of the acid. In the case of the

chloride $BiCl_3,H_2O$ and the **nitrate** $Bi(NO_3)_3,5H_2O$, the actions taking place are:

$$BiCl_3 + 2H_2O \rightleftarrows Bi(OH)_2Cl + 2HCl,$$
$$Bi(NO_3)_3 + 2H_2O \rightleftarrows Bi(OH)_2NO_3 + 2HNO_3.$$

The former of these products, when dried, loses a molecule of water, giving the **oxychloride** $BiOCl$. The **oxynitrate** $Bi(OH)_2NO_3$ is much used in medicine, for the treatment of some forms of indigestion, under the name of "subnitrate of bismuth." It is often contained in face powders.

The brownish-black **trisulphide** Bi_2S_3 may be obtained by direct union of the elements, or by precipitation with hydrogen sulphide. This sulphide is not affected by solutions of ammonium sulphide or of potassium sulphide. It differs, therefore, markedly from the sulphides of arsenic and antimony in its behavior.

The Family as a Whole

The elements themselves change progressively in physical properties as the atomic weight increases. Nitrogen is a gas which with sufficient cooling yields a white solid, phosphorus an almost white or a red solid, and arsenic, antimony, and bismuth are metallic in appearance. The first combines directly with hydrogen, the next three give hydrides indirectly, and the last does not unite with hydrogen at all. The hydride of nitrogen combines with water to form a base, while the other hydrides show no such tendency. Ammonia unites with acids, including those of the halogens, to form salts; phosphine with the hydrogen halides only; the others do not combine with acids at all. As regards their metallic properties, in the chemical sense, nitrogen and phosphorus do not by themselves form positive ions, and furnish us therefore with no salts whatever. Arsenic gives a trivalent positive ion, which is found in solutions of the halides only. It forms no normal sulphates, nitrates, or other salts. Antimony and bismuth both give trivalent positive ions. The sulphates, nitrates, etc., of antimony, however, are readily decomposed by water with precipitation of the hydroxide. The salts of bismuth, on the other hand, do not readily give the pure hydroxide with water, although they are easily hydrolyzed to basic salts.

The halogen compounds of nitrogen and phosphorus are completely hydrolyzed by water, and do not persist when any water is present, even when excess of the halogen acid is used. The halogen compounds of arsenic are completely hydrolyzed by cold water, but exist in solution in presence of excess of the acids. The halogen compounds of antimony and bismuth are incompletely hydrolyzed by cold water.

Each element gives a trioxide and a pentoxide. With nitrogen these are acid-forming, being the anhydrides of nitrous and nitric acids. With phosphorus the trioxide and the pentoxide are anhydrides of acids. With arsenic the trioxide is basic towards the halogen acids, and is the first example of a basic oxide which we encounter in this group. The pentoxide, however, is acid-forming. The trioxide of antimony is mainly base-forming, although it is feebly acid-forming also. The pentoxide is acid-forming. The trioxide of bismuth is base-forming exclusively, and the pentoxide has no derivatives.

These statements, which could easily be expanded, are sufficient to show that when the periodic law is borne in mind it furnishes valuable aid in systematizing the chemistry of a group like this.

Analytical Reactions of Arsenic, Antimony, and Bismuth. — The ions which are most frequently encountered are As^{+++}, Sb^{+++}, Bi^{+++}, $AsO_4^{\equiv}$, and $AsO_3^{\equiv}$. The first three, with hydrogen sulphide, give colored sulphides which are not affected by dilute acids. The sulphides of arsenic and antimony are separable from the sulphide of bismuth by solution in yellow ammonium sulphide. Marsh's test enables us to recognize the presence of traces of compounds of arsenic and antimony. Oxygen compounds of arsenic, when heated with carbon, give a volatile, metallic-looking deposit of arsenic.

VANADIUM, COLUMBIUM, TANTALUM

Of these elements, **vanadium** is less uncommon than the others. It is found in rather complex compounds. When these are heated with soda and sodium nitrate, **sodium metavanadate** $NaVO_3$ is formed, and can be extracted with water. The element forms several **chlorides**, such as VCl_2, VCl_3, VCl_4, $VOCl_3$, and five **oxides**, V_2O, VO, V_2O_3, VO_2, and V_2O_5. The element has very feeble base-forming properties, and gives only a few unstable salts. Ferrovanadium, an alloy, is used in making vanadium steel.

Columbium (or niobium), first discovered and named by Hatchett (1801), and **tantalum** possess feeble base-forming properties, their chief compounds being the columbates and tantalates.

Exercises. — 1. How do you account for the fact that the molecular weight of arsenic at 644° is not exactly 300, and why is 308.4 ÷ 4 not accepted as the atomic weight?

2. Formulate the series of changes involved in the solution of arsenic trioxide and the interaction of hydrochloric acid with the arsenious acid so formed (*cf.* p. 272).

3. What is the full significance of the fact that arsenic pentasulphide may be precipitated by hydrogen sulphide from a solution of arsenic acid in hydrochloric acid? Make the equation.

4. To what classes of chemical changes do the interactions of arsenious sulphide and antimony trisulphide with yellow ammonium sulphide belong?

5. Construct equations showing the interaction of, (*a*) oxygen and arsenical pyrites, (*b*) chlorine-water and arsenic, (*c*) the dehydration of orthoarsenic acid, (*d*) potassium hydroxide and arsenic trioxide, (*e*) concentrated nitric acid and antimony, (*f*) potassium bitartrate and antimony trioxide, (*g*) acids and ammonium orthosulphantimoniate.

6. How should you set about making Schlippe's salt?

CHAPTER XLIII

THE CHROMIUM FAMILY. RADIUM

THE chromium (Cr, at. wt. 52) family includes **molybdenum** (Mo, at. wt. 96), **tungsten** (W, at. wt. 184), and **uranium** (U, at. wt. 238.2), and occupies the seventh column of the periodic table along with the sulphur and selenium family.

The Chemical Relations of the Family. — The features which are common to the four elements are also those which affiliate them most closely with their neighbors on the right side of the column. They yield oxides of the forms CrO_3, MoO_3, WO_3, and UO_3, which, like SO_3, are acid anhydrides, and show the elements to be sexivalent. They give also acids of the form H_2XO_4, such as chromic acid H_2CrO_4. These acids correspond to sulphuric acid, and their salts, for example the chromates, resemble the sulphates.

Aside from the chromates, the first element forms also two basic hydroxides $Cr(OH)_2$ and $Cr(OH)_3$, from which the numerous chromous (Cr^{++}) and chromic (Cr^{+++}) salts are derived. Uranium is base-forming, as well as acid-forming. Molybdenum and tungsten are not base-forming elements.

CHROMIUM Cr

The Chemical Relations of the Element. — Chromium gives four classes of compounds, and most of them are colored substances (Gk. χρῶμα, color). The chromates are derived from chromic acid H_2CrO_4, which, however, is itself unstable, and leaves the anhydride when the solution is evaporated. The oxide and hydroxide in which the element is trivalent, namely Cr_2O_3 and $Cr(OH)_3$, are weakly basic and still more weakly acidic. Hence we have chromic salts such as $CrCl_3$ and $Cr_2(SO_4)_3$ which are somewhat hydrolyzed, but no carbonate, and no sulphide which is stable in water. The compounds in which the same hydroxide acts as an acid are the chromites, and are derived from the less completely hydrated form of the oxide $CrO(OH)$. Potassium chromite $K.CrO_2$ is more easily hydrolyzed, however, than is potassium zincate or potassium aluminate. Finally, the chromous salts such as $CrCl_2$ and $CrSO_4$ correspond to chromous hydroxide $Cr(OH)_2$ in which the element is bivalent. This hydroxide is more distinctly basic than is chromic hydroxide, and forms a carbonate and sulphide which can be precipitated in aqueous solution.

Occurrence and Isolation. — Chromium is found chiefly in ferrous chromite $Fe(CrO_2)_2$, which constitutes the mineral chromite, and in crocoisite $PbCrO_4$, which is chromate of lead. It was first discovered in the latter mineral by Vauquelin (1797). The metal is easily made by reduction of the oxide with aluminium filings by Goldschmidt's method (p. 556).

Physical and Chemical Properties. — Chromium is a white, crystalline, very hard metal (m.-p. 1520°). It does not tarnish, but when heated it burns in oxygen, giving the green chromic oxide Cr_2O_3. It seems to exist in two states, an active and a passive one, the relations of which are still somewhat obscure. A fragment which has been made by the Goldschmidt method, or has been dipped in nitric acid, is passive, and does not displace hydrogen from hydrochloric acid. When, however, the specimen is warmed with this acid, it begins to interact, and thereafter behaves as if it lay between zinc and cadmium in the electromotive series. If left in the air, it slowly becomes inactive again.

Tin and iron with hydrochloric acid form stannous and ferrous chlorides respectively, because the higher chlorides, if present, would be reduced by the active hydrogen (p. 360). Here, for the same reason, chromous chloride and not chromic chloride is formed:

$$Cr + 2HCl \rightarrow CrCl_2 + H_2, \quad \text{or} \quad Cr + 2H^+ \rightarrow Cr^{++} + H_2.$$

Chromium is used in making chrome-steel, for armorplate. The strange alloys, which, although composed of active metals, are not attacked by acids (even boiling nitric acid), usually contain chromium (*e.g.*, 60% Cr, 36% Fe, 4% Mo).

DERIVATIVE OF CHROMIC ACID

Potassium Chromate K_2CrO_4. — This and the sodium salt, or rather the corresponding dichromates (see below), are made directly from chromite, and form the starting-point in the preparation of the other compounds of chromium. The finely powdered mineral is mixed with potash and limestone, and roasted. The lime is employed chiefly to keep the mass porous and accessible to the oxygen of the air, the potassium compounds being easily fusible:

$$4Fe(CrO_2)_2 + 8K_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8K_2CrO_4 + 8CO_2.$$

The iron is oxidized to ferric oxide, and the chromium passes from the state of chromic oxide in the chromite (FeO,Cr_2O_3) to that of chromic anhydride in the potassium chromate (K_2O,CrO_3). Thus, more insight is given into the nature of the action by the equation:

$$4(FeO,Cr_2O_3)+8(K_2O,CO_2)+7O_2\rightarrow 2Fe_2O_3+8(K_2O,CrO_3)+8CO_2.$$

The cinder is treated with hot potassium sulphate solution. This interacts with the calcium chromate, which is formed at the same time, giving insoluble calcium sulphate:

$$CaCrO_4 + K_2SO_4 \leftrightarrows CaSO_4 \downarrow + K_2CrO_4.$$

The whole of the potassium chromate goes into solution.

Potassium chromate is pale-yellow in color, gives anhydrous, rhombic crystals like those of potassium sulphate, and is very soluble in water (61 : 100 at 10°).

Sodium chromate $Na_2CrO_4,10H_2O$ is made by using sodium carbonate in the process just described.

The Dichromates. — When a solution of potassium sulphate is mixed with an equivalent amount of sulphuric acid, potassium bisulphate is obtainable by evaporation: $K_2SO_4 + H_2SO_4 \rightarrow 2KHSO_4$. The *dry* acid salt, when *heated*, loses water (p. 286), giving the pyrosulphate (or disulphate): $2KHSO_4 \rightleftarrows K_2S_2O_7 + H_2O$, but the latter, when redissolved, returns to the condition of acid sulphate. The second action is instantly reversed in presence of water. Now, when an acid is added to a chromate we should expect the chromic acid H_2CrO_4, thus liberated, to interact, giving an acid chromate (say, $KHCrO_4$). No acid chromates are known, however, and instead of them, pyrochromates or dichromates are produced, with elimination of water. In other words, the second of the above actions is not appreciably reversible in presence of water when chromates are in question:

$$\begin{array}{l} K_2CrO_4 + H_2SO_4 \rightarrow (H_2CrO_4) + K_2SO_4. \\ K_2CrO_4\,(+\,H_2CrO_4) \rightarrow K_2Cr_2O_7 + H_2O. \\ \hline 2K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + H_2O + K_2SO_4. \end{array} \qquad (1)$$

In terms of the ionic hypothesis, $S_2O_7^{=}$ is unstable in water, and interacts with the OH^- ion it contains, giving water and sulphate-ion, while $Cr_2O_7^{=}$ is stable in water and is formed from the interaction of water and chromate-ion:

$$\begin{array}{l} S_2O_7^{=} + 2OH^- \leftrightarrows H_2O + 2SO_4^{=}, \\ Cr_2O_7^{=} + 2OH^- \leftrightarrows H_2O + 2CrO_4^{=}. \end{array} \qquad (2)$$

The dichromates of potassium and sodium are made by adding sulphuric acid to the crude solution of the chromate obtained from chromite (p. 597). They crystallize when the liquid cools, and the mother-liquor, containing the potassium sulphate and undeposited dichromate, is used for extracting a fresh portion of cinder. As the dichromates are much less soluble than the chromates, they crystallize from less concentrated solutions, and can therefore be obtained in purer condition. For this reason the extract is always treated for dichromate.

Potassium dichromate $K_2Cr_2O_7$ (or K_2CrO_4,CrO_3) crystallizes in asymmetric tables of orange-red color. Its solubility in water is 8 : 100 at 10° and 12.5 : 100 at 20°. **Sodium dichromate** $Na_2Cr_2O_7, 2H_2O$ forms red crystals also, and its solubility is 109 : 100 at 15°. This salt is now cheaper than potassium dichromate, and has largely displaced the latter for commercial purposes.

Chemical Properties of the Dichromates. — 1. When concentrated sulphuric acid is added to a strong solution of a dichromate (or chromate), **chromic anhydride** CrO_3 separates in red needles:

$$Na_2Cr_2O_7 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + 2CrO_3\downarrow.$$

2. Although a dichromate lacks the hydrogen, it is essentially of the nature of an acid salt, just as SbOCl lacks hydroxyl, but is

essentially a basic salt. Hence, when potassium hydroxide is added to a solution of potassium dichromate, potassium chromate is formed:

$$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O.$$

The solution changes from red to yellow, and the chromate is obtained by evaporation. In this way the pure alkali chromates are made.

3. By addition of potassium dichromate to a solution of a salt of a metal whose chromate is insoluble, the chromate and *not* the dichromate is precipitated. This occurs in consequence of the fact that there is always a little hydrogen-ion and $CrO_4^{=}$ (equation (2), above) in the solution of the dichromate:

$$2Ba(NO_3)_2 + K_2Cr_2O_7 + H_2O \rightleftarrows 2BaCrO_4 \downarrow + 2KNO_3 + 2HNO_3.$$

Being essentially an acid salt, the dichromate produces a salt and an acid, as any acid salt would do. For example:

$$Ba(NO_3)_2 + KHSO_4 \rightleftarrows BaSO_4 \downarrow + KNO_3 + HNO_3.$$

4. The dichromates of potassium and sodium melt when heated and, at a white heat, decompose, giving the chromate, chromic oxide, and free oxygen. To make the equation, we note that the dichromate, for example $K_2Cr_2O_7$, may be written as K_2CrO_4,CrO_3, and the CrO_3, if alone, will decompose thus: $2CrO_3 \rightarrow Cr_2O_3 + 3O$. Since the product must contain a multiple of O_2, the equation is:

$$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2.$$

5. With free acids the dichromates give powerful oxidizing mixtures, in consequence of their tendency to form chromic salts. Since the former correspond to the oxide CrO_3 and the latter to Cr_2O_3, the passage from the former to the latter must furnish 3O for every $2CrO_3$ transformed. In dilute solutions, unless a body capable of being oxidized is present, no actual decomposition, beyond the liberation of chromic acid,* occurs. When concentrated hydrochloric acid is used, this acid itself suffers oxidation:

$$\begin{array}{l} K_2Cr_2O_7 + 8HCl \rightarrow 2KCl + 2CrCl_3 + 4H_2O\ (+ 3O). \\ (3O) \quad + 6HCl \rightarrow 3H_2O + 3Cl_2. \\ \hline K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2. \end{array}$$

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* Not shown as a distinct stage in the subsequent equations.

When sulphuric acid is employed, an oxidizable substance such as hydrogen sulphide (*cf.* p. 270), sulphurous acid, or alcohol must be present, if the dichromate is to be reduced:

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O(+3O) \qquad (1)$$

$$(3O) + 3H_2SO_3 \rightarrow 3H_2SO_4 \qquad (2)$$

$$\text{or} \quad (3O) + \underset{\text{[alcohol]}}{3C_2H_5OH} \rightarrow \underset{\text{[aldehyde]}}{3C_2H_4O} \uparrow + 3H_2O \qquad (2')$$

In each case the usual summation of (1) and (2), with omission of the 3O, gives the equation for the whole action. When (1) is dissected, $K_2O,2CrO_3$ giving $Cr_2O_3,3SO_3 + 3O$ is found to be its essential content. In practice, this sort of action is used for the purpose of making chromic salts, and for its oxidizing effects, as in the preparation of aldehyde and in the dichromate battery.

Other Uses of Dichromates. — When paper is coated with gelatine containing a soluble chromate or dichromate and, after being dried, is exposed to light, chromic oxide is formed by reduction, and combines with the gelatine. This product will not swell up or dissolve in tepid water, as does pure gelatine. This action is used in many ways for purposes of artistic reproduction. Thus, if the gelatine mixture is made up with lampblack and, after the coating has dried, is covered with a negative and exposed to light, the parts which were protected from illumination may afterwards be washed away, while the **carbon print** remains. The gelatine layer can be transferred to wood or copper before washing. When materials of different colors are substituted for the lampblack, prints of any desired tint may be made by the same process.

Sodium dichromate is used, instead of tan-bark, in **tanning** kid and glove leathers. A reducing agent is employed to precipitate chromic hydroxide $Cr(OH)_3$ in the leather. Its use diminishes the time required for the process from 8 or 10 months to a few hours. The hide is a mixture of colloidal materials, and the hydroxide is adsorbed.

Insoluble Chromates. — A number of chromates, formed by precipitation with a solution of a soluble chromate or dichromate, are familiar. Thus, **lead chromate** $PbCrO_4$ is used as a yellow pigment. By treatment with limewater it gives a basic salt of brilliant orange color — **chrome-red** Pb_2OCrO_4. Salts of calcium give a yellow, hydrated **calcium chromate** $CaCrO_4,2HO_2$ analogous to gypsum, and, like it, perceptibly soluble in water (0.4 : 100 at 14°). **Barium chromate** $BaCrO_4$ is also yellow. It interacts with active acids to form the dichromate, and passes into solution. It is not soluble enough to be attacked by acetic acid. **Strontium chromate** $SrCrO_4$, however, is soluble in acetic acid. **Silver chromate** Ag_2CrO_4 is red, and interacts easily with acids. It will be observed that there is a close correspondence between the relative solubilities (see Table) of the chromates and the sulphates.

Chromic Anhydride CrO_3. — This oxide is made as described above (par. 1, p. 598), and is often called chromic acid. It is soluble in water, and combines with the latter to some extent, giving dichromic acid $H_2.Cr_2O_7$. In a solution acidified with an active acid it is much used as an oxidizing agent for organic substances. It interacts with acids in the same way as do the dichromates, giving chromic salts and furnishing oxygen to the oxidizable body. When heated by itself, it loses oxygen readily, and yields the green chromic oxide: $4CrO_3 \rightarrow 2Cr_2O_3 + 3O_2$.

Chromyl Chloride CrO_2Cl_2. — This compound corresponds to sulphuryl chloride SO_2Cl_2, and is made by distilling a dichromate with a chloride and concentrated sulphuric acid:

$$K_2Cr_2O_7 + 4KCl + 3H_2SO_4 \rightarrow 2CrO_2Cl_2 \uparrow + 3K_2SO_4 + 3H_2O.$$

The hydrochloric acid liberated from the chloride may be supposed to interact with chromic acid from the dichromate:

$$CrO_2(OH)_2 + 2HCl \rightarrow CrO_2Cl_2 + 2H_2O.$$

Chromyl chloride is a red liquid, boiling at 118°. It fumes strongly in moist air, being hydrolyzed by water. This action is the reverse of that shown in the last equation. The corresponding bromine and iodine compounds are unstable, and when a bromide or iodide is treated as described above, the halogens are liberated by oxidation, and no volatile compound of chromium appears. Hence, when an unknown halide is mixed with potassium dichromate and sulphuric acid, and distilled, and the vapors are caught in ammonium hydroxide, the finding of a chromate in the distillate demonstrates the existence of a chloride in the original substance:

$$CrO_2Cl_2 + 4NH_4OH \rightarrow (NH_4)_2CrO_4 + 2NH_4Cl + 2H_2O.$$

This action is used as a test for the presence of traces of chlorides in large amounts of bromides or iodides.

CHROMIC AND CHROMOUS COMPOUNDS

Chromic Chloride. — A hydrated chloride $CrCl_3,6H_2O$ is obtained by treating the hydroxide $Cr(OH)_3$ with hydrochloric acid and evaporating. When heated, this hydrate is hydrolyzed, and chromic oxide remains. The anhydrous chloride $CrCl_3$ is formed by sublimation, as a mass of brilliant, reddish-violet scales, when chlorine is led over heated metallic chromium. In this form the substance dissolves with extreme slowness, even in boiling water, but in presence of a trace of chromous chloride or stannous chloride it is easily soluble. The solution is green, as are all solutions of chromic salts after they have been boiled, but on standing in the cold, bluish crystals of $CrCl_3,6H_2O$ are deposited. These give a violet solution containing $Cr^{+++} + 3Cl^-$, but boiling reproduces the green color. The green material can also be obtained in crystals as a hexahydrate, and is therefore isomeric (p. 421) with the violet variety. With the green isomer, in cold solution, silver nitrate precipitates at first only one-third of the chlorine as silver chloride.

Chromic Hydroxide. — When ammonium hydroxide is added to a solution of a chromic salt, a hydrated hydroxide of pale-blue color, $2Cr(OH)_3,H_2O$, is thrown down. This interacts with acids, giving chromic salts. It also dissolves in potassium and sodium hydroxides to form green solutions of **chromites** of the form $KCrO_2$. When the solutions of the alkali chromites are boiled, the free chromic hydroxide, present in consequence of hydrolysis, is converted into a greenish, less completely hydrated, and less soluble variety. This begins to come out as a precipitate, and soon the whole action is reversed. Insoluble chromites, such as that of iron $Fe(CrO_2)_2$, are found in nature. Many of them, like $Zn(CrO_2)_2$ and $Mg(CrO_2)_2$, may be formed by fusing the oxide of the metal with chromic oxide; the action being similar to that used in making zincates (p. 529) and aluminates (p. 557). The hydroxide is used as a mordant (p. 565) and is the active substance in the chrome-tanning process (p. 600).

Chromic Oxide Cr_2O_3. — This oxide is obtained as a green, infusible powder by heating the hydroxide; or, more readily, by heating dry ammonium dichromate; or by igniting potassium dichromate with sulphur and washing the potassium sulphate out of the residue:

$$(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3,$$
$$K_2Cr_2O_7 + S \rightarrow K_2SO_4 + Cr_2O_3.$$

Chromic oxide is not affected by acids, but may be converted into the sulphate by fusion with potassium bisulphate. It is used for making green paint, and for giving a green tint to glass. When the oxide, or any of the chromic salts, is fused with a basic substance such as an alkali carbonate, it passes into the form of a chromate, absorbing the necessary oxygen from the air. If an alkali nitrate or chlorate is added, the oxidation goes on more quickly. The alkaline solution of the chromites may be oxidized, for example by adding chlorine or bromine, and chromates are formed.

Chromic Sulphate $Cr_2(SO_4)_3,15H_2O$. — This salt crystallizes in reddish-violet crystals, and may be made by treating the hydroxide with sulphuric acid. When mixed with potassium sulphate, it gives reddish-violet, octahedral crystals of **chrome-alum** (*cf.* p. 558), $K_2SO_4,Cr_2(SO_4)_3,24H_2O$. This double salt is most easily obtained by reducing potassium dichromate in dilute sulphuric acid by means of sulphurous acid (p. 600), and allowing the solution to crystallize. The solution of the crystals, either of the pure sulphate or of the alum, is bluish-violet (Cr^{+++}), but when boiled becomes green. The green compound is formed by hydrolysis and is gummy and uncrystallizable. It even yields products which do not show the presence either of the Cr^{+++} or the $SO_4^{=}$ ion. It seems to be formed thus:

$$2Cr_2(SO_4)_3 + H_2O \rightleftarrows Cr_4O(SO_4)_4.SO_4 + H_2SO_4.$$

The green materials revert slowly to the violet ones by reversal of the above action when the solution remains in the cold, and so crystals of the sulphate or of the alum are obtainable from the green solutions.

Chromous Compounds. — By the interaction of chromium with hydrochloric acid, or by reducing chromic chloride in a stream of hydrogen, **chromous chloride** $CrCl_2$ is formed. The anhydrous salt is colorless, and its solution is light blue (Cr^{++}). Like stannous chloride, it is very easily oxidized by the air, a solution of it containing excess of hydrochloric acid being used in the laboratory to absorb oxygen:

$$4CrCl_2 + 4HCl + O_2 \rightarrow 4CrCl_3 + 2H_2O.$$

Chromous hydroxide $Cr(OH)_2$ is obtained as a yellow precipitate when alkalies are added to the chloride. With sulphuric acid it gives **chromous sulphate** $CrSO_4,7H_2O$, which is one of the vitriols (p. 529).

Analytical Reactions of Chromium Compounds. — The chromic salts give the bluish-violet chromic-ion Cr^{+++}, or the green complex cations, and may be recognized in solution by their color. The chromates and dichromates give the ions $CrO_4^{=}$ and $Cr_2O_7^{=}$, which are yellow and red respectively. From chromic salts, alkalies and ammonium sulphide precipitate the bluish-green hydroxide, and carbonates give a basic carbonate which is almost completely hydrolyzed to hydroxide. By fusion with sodium carbonate and sodium nitrate, they yield a yellow bead containing the chromate. The chromates and dichromates are recognized by the insoluble chromates which they precipitate, and by their oxidizing power when mixed with acids. All compounds of chromium give a green borax bead containing chromic borate, and this bead differs from that given by compounds of copper (*cf.* p. 510), both in tint and in being unreducible.

Molybdenum, Tungsten, Uranium

Molybdenum. — This element is found chiefly in wulfenite $PbMoO_4$ and molybdenite MoS_2. The latter resembles black lead (graphite), and its appearance suggested the name of the element (Gk. μολύβδαινα, lead). The molybdenite is converted by roasting into **molybdic anhydride** MoO_3. When this is treated with ammonium hydroxide, or with sodium hydroxide, **ammonium molybdate** $(NH_4)_2MoO_4$ or **sodium molybdate** $Na_2MoO_4,10H_2O$ is obtained. The **metal** itself is liberated by reducing the oxide or chloride with hydrogen. When pure it is a silvery metal and, like iron (*q.v.*), takes up carbon and shows the phenomena of tempering. The **oxides** Mo_2O_3, MoO_2, and MoO_3 are known, but the lower oxides are not basic. The **chlorides** Mo_3Cl_6, $MoCl_3$, $MoCl_4$, and $MoCl_5$ have been made. The chief use of molybdenum compounds in the laboratory is in **testing for** and estimating **phosphoric acid.** When a little of a phosphate is added to a solution of ammonium molybdate in nitric acid, and the mixture is warmed, a copious yellow precipitate of a **phosphomolybdate of ammonium** $(NH_4)_3PO_4,11MoO_3,6H_2O$ is formed. The compound is soluble in excess of phosphoric acid and in alkalies, but not in dilute mineral acids.

Tungsten. — The minerals scheelite $CaWO_4$ and wolfram $[Fe,Mn]WO_4$ are tungstates of calcium and of iron and manganese, respectively. By fusion of wolfram with sodium carbonate and extraction with water, **sodium tungstate** $Na_2WO_4,2H_2O$ is secured. It is used as a mordant and for rendering muslin fireproof. Acids precipitate **tungstic acid** H_2WO_4,H_2O from solutions of this salt. The element gives the **oxides** WO_2 and WO_3, the latter being formed by ignition of tungstic acid. The **chlorides** WCl_2, WCl_4, WCl_5, and WCl_6 are known, the last being formed directly, and the others by reduction.

The metal has important **uses,** and the annual production is greater than the total of all the metals which follow it in the list on p. 436. The metal (sp. gr. 19.6) can be liberated by reduction of the oxide by hydrogen or by carbon. It has a higher melting point (3540°) than any other metal and, on this account, and because it is less volatile than carbon, is now used for filaments in electric lamps. A carbon filament also requires 3.25 watts per candle power while a tungsten filament uses only 1.25 watts per 1 c. p. The powdered metal obtained by reduction can be pressed into wire form and then rolled while strongly heated by an electric current until a compact wire is obtained. The metal can also be obtained in massive form by reducing the oxide with aluminium, provided the crucible and mixture are heated strongly in advance. In 1914, in the United States alone, about a hundred million tungsten lamps were manufactured. Shop work has been almost revolutionized by the use of tungsten steel tools, which can be used at high speed and, even when thus heated red hot by friction, retain their temper. Tungsten steel contains tungsten (16 to 20%), carbon (0.55 to 0.75%), chromium (2.5 to 5%), and vanadium (0.35 to 1.5%).

Uranium. — Pitchblende, which contains the oxide U_3O_8 along with smaller amounts of many other elements, is found mainly in Joachimsthal (Bohemia) and in Cornwall. Carnotite, a uranate and vanadate of potassium $K_2O,2UO_3,V_2O_5,3H_2O$ occurs in Colorado. Pitchblende is roasted with lime, the calcium uranate $CaUO_4$ thus formed is decomposed with sulphuric acid, giving uranyl sulphate UO_2SO_4. When excess of sodium carbonate is added to the solution of the latter, the foreign metals are precipitated and **sodium diuranate** $Na_2U_2O_7,7H_2O$, which is also thrown down, dissolves in the excess as Na_2UO_4.

After filtration, the diuranate of sodium is reprecipitated by neutralizing with sulphuric acid and boiling. This salt is used in making **uranium glass,** which shows a yellowish-green fluorescence. The property is due to the fact that the wave-lengths of part of the invisible, ultra-violet rays of the sunlight are lengthened, and a greenish light is therefore in excess. The **oxides** are UO_2 a basic oxide, U_2O_3, U_3O_8 the most stable oxide, UO_3 uranic anhydride, and UO_4 a peroxide.

When the oxide UO_2 is treated with acids, it gives uranous salts such as **uranous sulphate** $U(SO_4)_2,4H_2O$. Uranic anhydride and uranic acid interact with acids, giving basic salts, such as $UO_2SO_4,3\frac{1}{2}H_2O$, and $UO_2(NO_3)_2,6H_2O$, which are named **uranyl sulphate, uranyl nitrate,** and so forth. They are yellow in color, with green fluorescence. Ammonium sulphide throws down the brown, unstable **uranyl sulphide** UO_2S from their solutions.

RADIOACTIVE ELEMENTS

Historical. — We have seen (p. 303) that in an evacuated tube, through which an electric discharge is passed, the "rays" emanating from the cathode (**cathode rays**) strike the anti-cathode and the glass beyond it. They produce in the glass a greenish-yellow, fluorescent light. These "rays" were discovered by Sir William Crookes (1878), and later were shown to consist of particles of negative electricity or **electrons,** each having a mass about $\frac{1}{1800}$ of an atom of hydrogen. Röntgen (1895) accidentally discovered that the fluorescent light (**X-rays**) could penetrate paper, flesh, and other materials composed of elements of low atomic weight and acted upon photographic plates. In 1896 Henri Becquerel observed that minerals containing uranium gave off a sort of radiation which could penetrate black paper that was opaque to ordinary light and reduce the silver bromide on a photographic plate placed beneath the paper. He also discovered that an electrometer (Fig. 133), in which the gold leaves had been caused to separate by charging with electricity, lost its charge rapidly when the uranium ore (or salt) was brought near (3–4 cm.) to the knob connected with the leaves. The uranium material rendered the air a conductor ("ionized" the air) and this effect permitted the escape of the electric charge, which otherwise would have been retained for a considerable time. In the quantitative measurement of radioactivity, we now compare the times required for the discharge of an electroscope by different specimens of radioactive matter. The presence of 10^{-12} g. of such matter can thus be detected.

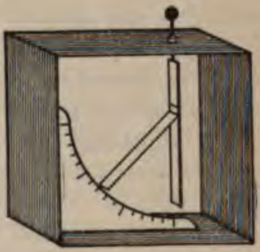


FIG. 133.

The radioactivity of every pure uranium compound is proportional to its uranium content. The *ores* are, however, relatively four times as active. This fact led M. and Mme. Curie, just after 1896, to the discovery that the pitchblende residues, from which practically all of the uranium had been extracted, were nevertheless quite active. About a ton of the very complex residues having been separated laboriously into the components, it was found that a large part of the radioactivity remained with the sulphate of barium. From this barium sulphate, a product free from barium, and at least one million times more active than uranium, was finally secured in the form of the bromide. The nature of the spectrum and the chemical relations of the element, now named **radium**, placed it with the metals of the alkaline earths. The ratio by weight of chlorine to radium in the chloride is 35.46 : 113, so that, on the assumption that the element is bivalent, its chloride is $RaCl_2$ and its atomic weight is 226. With this value it occupies a place formerly vacant in the periodic table.

In 1910 Mme. Curie obtained metallic radium by electrolyzing a solution of radium chloride, using a mercury cathode, and expelling the mercury by distillation. It was a white metal (m.-p. 700°) which, like calcium, quickly tarnished in the air and displaced hydrogen from water.

The Nature of the "Rays." — Many properties show that the "rays" emitted by compounds of uranium and of radium are of three kinds. They are most sharply distinguished from one another when allowed to pass through a powerful magnetic field. The **alpha-rays** are positively charged and are bent in one direction while the **beta-rays** are negative and are bent in the other. The **gamma-rays** are not affected.

The **alpha-rays** are atoms of **helium** (p. 336) thrown off in straight lines with varying initial velocities, averaging about one-tenth that of light (say, 30,000 kilometers per second. The α-particles from Ra-C, *e.g.*, 19,220 kilom. per sec.). Each such atom bears a double positive charge (the unit being the charge on a univalent positive ion), and a delicate electroscope readily indicates the entrance of a single atom. These alpha-particles, being each four times as heavy as an atom of hydrogen, plough their way *through* tens of thousands of air-molecules and usually go about 3–8 cm. before being stopped. The emission of atoms of helium can be detected by means of Crookes **spintharoscope** (Fig. 134). The particle of radium bromide is at *B*, and some of the charged helium atoms strike a surface *C* covered with zinc sulphide, producing faint flashes of light. The lens *A* magnifies the flashes and the latter can be seen in a dark room after the eye has become thoroughly rested (15–20 minutes). The helium gas given off by radium compounds was collected by Soddy working with Ramsay and identified, and its rate of production was measured. The amount was equal to 158 cubic mm. per 1 g. of radium per year.

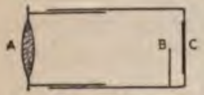


Fig. 134.

The alpha-particles, in passing through the air-molecules, ionize the air, and the ionized air has the same power that dust possesses (p. 333) of affording nuclei on which moisture can condense. Hence, when a particle of a radium compound is supported in a flask containing air saturated with moisture, and the air is suddenly cooled by expansion, the paths of the particles become lines of fog. With powerful illumination, the fog-tracks (Fig. 135) can be photographed (Wilson), and the lengths of the paths can be measured.

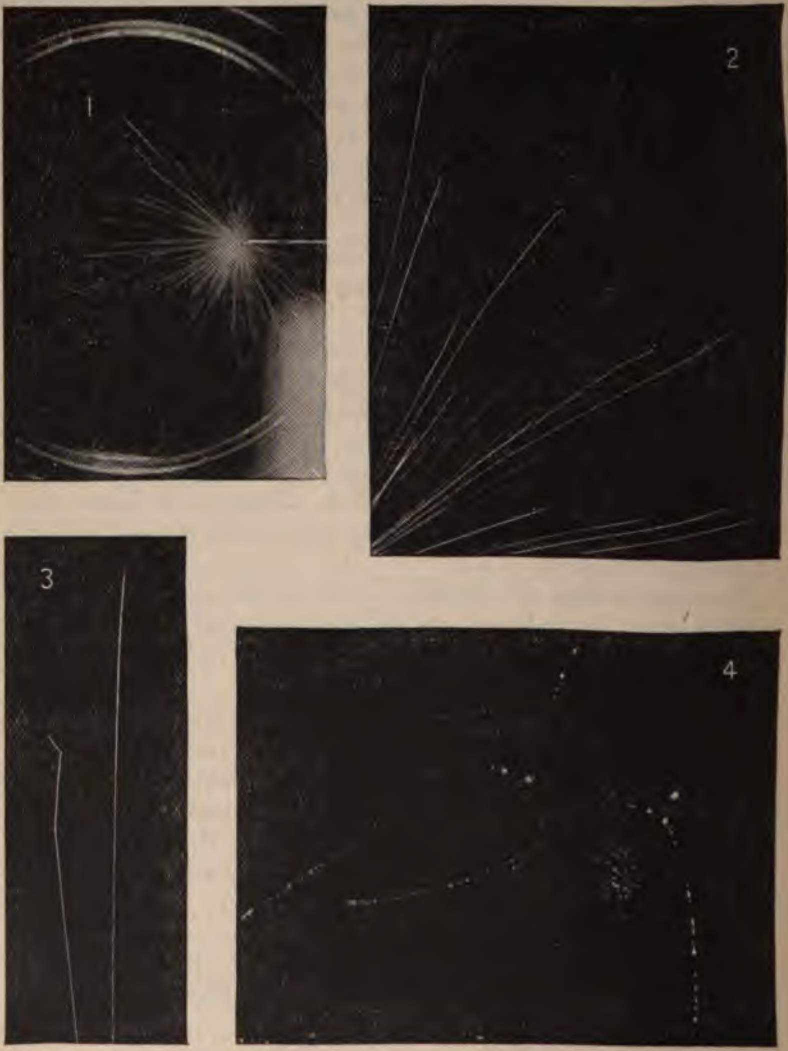
The **beta-particles** are **electrons** (p. 303), or unit charges of negative electricity, and are shot out with a velocity approaching that of light (300,000 kiloms. per sec.). They are therefore identical with cathode rays, but move many times more rapidly. Being very light (weight, $\frac{1}{1800}$ of an atom of hydrogen), their paths, although straight at first, soon become tortuous owing to collisions with the relatively massive air-molecules. Half of them are lost after going about 4 cm. Their fog tracks are fainter than are those of the α-particles and extremely tangled. Being much lighter than α-particles, their paths are actually coiled into circles or spirals by a magnetic field.

The **gamma-rays** are identical with X-rays (vibrations in the ether of short wave-length, p. 303), and are presumably produced like the latter by the impacts of the electrons on the surrounding matter.

The helium atoms are almost all stopped by a sheet of paper or by aluminium foil 0.1 mm. thick. The electrons have greater penetrating power, many passing through gold-leaf, but being practically all destroyed by a sheet of aluminium 1 cm. thick. The gamma-rays (X-rays), however, are able to penetrate relatively thick layers of metals and other materials of low atomic weight.

One of the most striking facts is that the stoppage by the air of so many rapidly moving particles results in the production of much heat. One gram of radium would produce about 120 cal. per hour.

Disintegration. — The emission of atoms of helium and of electrons was first explained by Rutherford (1902–3), then of McGill University, Montreal, as being due to the spontaneous



FOG-TRACKS FROM RADIUM (C. T. R. WILSON)

1, 2. Paths of helium atoms. 3. Part of 2, enlarged. 4. Paths of electrons.

Fig. 135.

disintegration of the atoms of uranium, radium, and other radioactive elements. Thus, Rutherford was the first to show that radium compounds produced a gaseous substance called the radium emanation (niton), which was the residue left after the emission of one atom of helium from an atom of radium. This gas was itself radioactive and underwent further disintegration, depositing a solid radioactive residue on bodies in contact with it. Furthermore, every known uranium ore contains radium (McCoy) and radium emanation (Boltwood) in amounts proportional to the uranium content. Also, after the radium has been removed, the pure uranium compound gives off at first only α-particles, but gradually recovers its whole radioactivity and is then found to contain radium emanation once more (Soddy). It thus appears that uranium is the starting point, and that the disintegration proceeds by steps, producing a number of different products. Each of these is formed from one such product and by disintegration furnishes another.

Unlike ordinary chemical change, the rate of disintegration is not affected by conditions. It can neither be started nor stopped at will. It is no more vigorous at 2000° than at $-200°$. Other changes occur *between* atoms, these *within* each atom.

The law, due also to Rutherford, describing the rate at which any one radioactive element disintegrates is simple. Only a certain fraction of the whole of any one specimen undergoes the change in unit time. Thus, as the total amount diminishes because of the change, the amount changing during the next unit of time, being a constant fraction of the whole, must be less. Hence an infinite time would be required for the complete disintegration of any one specimen. For convenience, therefore, it is sometimes the custom to give as a specific property of each radioactive element the time required for the decay of half its amount and therefore the loss of half of its radioactivity. More usually, the property given is the one called **the average life of the element.** The value of this is equal to the inverse of the fraction disintegrating per unit time, and is about 1.44 times the period of half change. Numerically it is the sum of the separate periods of future existence of all the atoms divided by the number of such atoms present at the starting point.

Radium emits helium atoms at the rate of 3.4×10^{10} per gram per second. From this fact, we can calculate its average life to be about 2400 years. Hence, if it were not continuously being produced (from uranium), the whole supply would have been exhausted long before the earth reached a habitable condition.

The Uranium Group of Radioactive Elements. — The following shows the various elements produced from uranium by successive disintegrations. When a helium atom or an electron is expelled, the fact is shown by the symbols He and ϵ, respectively. The first number below each element is the average life of that member of the series (y = year, d = day, h = hour, m = minute, s = second). The second number is the atomic weight, obtained by subtracting from the at. wt. of uranium (238.2) the weight (4) of each helium atom emitted.

$$\underset{\substack{8\times10^{9}\text{ y.}\\238.2}}{\text{U}_1} \rightarrow \mathbf{He}+\underset{\substack{35.5\text{ d.}\\234.2}}{\text{U-X}_1} \rightarrow \epsilon+\underset{\substack{1.65\text{ m.}\\234.2}}{\text{U-X}_2} \rightarrow \epsilon+\underset{\substack{3\times10^{6}\text{ y.}\\234.2}}{\text{U}_2} \rightarrow \mathbf{He}+\underset{\substack{2\times10^{5}\text{ y.}\\230.2}}{\text{Ionium}}$$

$$\rightarrow \mathbf{He}+\underset{\substack{2440\text{ y.}\\226}}{\text{Ra}} \rightarrow \mathbf{He}+\underset{\substack{5.55\text{ d.}\\222}}{\text{Niton}} \rightarrow \mathbf{He}+\underset{\substack{4.3\text{ m.}\\218}}{\text{Ra-A}} \rightarrow \mathbf{He}+\underset{\substack{38.5\text{ m.}\\214}}{\text{Ra-B}}$$

$$\rightarrow \epsilon+\underset{\substack{28.1\text{ m.}\\214}}{\text{Ra-C}} \rightarrow \epsilon+\underset{\substack{10^{-6}\text{ s.}\\214}}{\text{Ra-C}_1} \rightarrow \mathbf{He}+\underset{\substack{24\text{ y.}\\210}}{\text{Ra-D}} \rightarrow \epsilon+\underset{\substack{7.2\text{ d.}\\210}}{\text{Ra-E}}$$

$$\rightarrow \epsilon+\underset{\substack{196\text{ d.}\\210}}{\text{Ra-F}} \rightarrow \mathbf{He}+\underset{206}{\text{Pb}}\text{ (end)}$$

A purified salt of uranium recovers half its activity in about three weeks, and reaches full equilibrium in from six months to a year. An equilibrium is attained when the speed at which each disintegration product is being formed is balanced by the equal speed with which it is passing into the next member of the series. The complex operations required for studying all the members of the series cannot be given here. It may be said, however, that a pure uranium salt in solution gives with ammonium carbonate a precipitate which is wholly soluble in excess of the reagent. After about a year, another portion of the same specimen leaves a slight precipitate which is insoluble in excess and contains the products of disintegration, chiefly U-X which was first obtained in this way by Crookes.

The radium emanation was shown by Ramsay to be one of the inert gases (p. 337), and was renamed niton. Its density was determined experimentally with a small sample, using a micro-balance capable of weighing to 1/500,000 mgm., and found to be 222.4 (density of oxygen = 32).

The end-product of the disintegration is lead, and all uranium ores contain lead. Lead from other sources gives a chloride $PbCl_2$ in which 207.20 parts of lead are combined with 2×35.46 parts of chlorine. The atomic weight 207.2 cannot, however, be reached by subtracting a whole number of atomic weights of helium from the atomic weight of uranium, the number 206 being obtained instead. Recently, lead chloride prepared from the lead found in various ores of uranium has been analyzed by Richards of Harvard, as well as, independently, by two other chemists, and the atomic weight of this lead was found to be from 206.4 to 206.8 in different samples. This lead chloride has properties *identical* with those of ordinary lead chloride and is, therefore, by definition, the same substance. Hence these investigations have revealed the first known exception to the law of definite proportions.

Since the initial (U) and final (Pb) materials are both electrically neutral, it must be assumed that at some stages more than one electron per atom is expelled. $8He^{++}$ are lost and therefore $16\epsilon^{-}$.

Additional Data.—The yield of radium is very small. 6000 kg. of pitchblende, after extraction of the uranium, yield about 2000 kg. of residue. This affords about 6 to 8 kg. of the mixture of radium and barium sulphates, from which 0.2 g. of pure radium bromide can be prepared.

One gram of uranium, after it has produced the equilibrium proportion of radium (about 3.2×10^{-7} g.), gives off helium at the rate of 1 c.c. in sixteen million years. Since the mineral fergusonite contains 26 c.c. of accumulated helium for every gram of uranium, the samples of this mineral must be at least 416 million years old.

The complete disintegration of 1 c.c. of niton to lead would deliver about seven million calories, but, of course, the liberation of the heat would be spread over a great length of time.

Chemical Actions of the "Rays." — The radiations which are most active in ionizing air and in acting upon photographic plates are the α-particles. These particles also cause the flashes of light when they encounter zinc sulphide. The radiations change the colors of minerals, including gems, and give a deep violet color to the glass tube containing the specimen. They also turn atmospheric oxygen in part into ozone and, in solution, produce traces of hydrogen peroxide in the water.

The radiations also destroy minute organisms and kill the cells of the skin, producing sores. They have been employed in the treatment of lupus and of superficial cancerous growths.

Other Radioactive Series. — Thorium, found as phosphate in monazite sand, is also radioactive and furnishes a series of disintegration products. The final material is a salt of lead. Analysis of the chloride of lead made from traces of the element found in all thorium minerals shows that the atomic weight (Soddy) is 208.4, while that of ordinary lead is 207.2. The atom of thorium (at. wt. 232.4) thus loses 6He ($= 6 \times 4 = 24$) during the disintegration. There are thus three chlorides of lead with identical properties, but different compositions, namely the common one $207.2 : 2 \times 35.46$, that from radium $206 : 2 \times 35.46$, and that from thorium $208.4 : 2 \times 35.46$.

Actinium and polonium are also radioactive elements, which have not yet been fully investigated. The former appears to be formed by a second, parallel, disintegration of U_1, and the latter in a similar way from Ra-E. Compounds of potassium and rubidium show traces of radioactivity.

Significance of Radioactivity. — The Brownian movement (p. 416) has revealed to us bodies intermediate between ordinary particles and single molecules, and has enabled us to estimate the actual weight of molecules. Radioactivity enables us to count charged molecules of helium as they enter the electroscope or produce flashes of light on zinc sulphide, and the fog-tracks permit us to follow their movements. There is thus now no question that molecules and atoms are real. Furthermore, we infer that all kinds of atoms are composed of a positive nucleus (p. 304) surrounded by electrons, although only the atoms of radioactive elements are unstable. The diameter of the positive nucleus of a hydrogen atom is calculated to be about $\frac{1}{1800}$ of that of an electron. Rutherford has confirmed this by actual measurement. The atom is thus no longer regarded as being solid and continuous in structure. It is mainly a vacuum, containing a few relatively very minute bodies possessing weight. The fact that α-particles are thus able to plough their way through molecules of oxygen and nitrogen, being diverted from a straight path only when they happen to pass very close to the positive nucleus (which, of course, repels the positive α-particles), is no longer mysterious.

Another interesting conclusion has been reached from the observation that niton is found in the soil and in many natural waters. Calculation shows that the heat given off by the disintegration of the amounts of radioactive matter known to exist in the crust of the earth is alone sufficient to account for the maintenance of the temperature of the planet. A globe of the size and material of the earth, possessing originally only heat energy, and cooling from a white hot condition to the temperature of interstellar space, would have passed through the stage of habitable temperatures in a much shorter time than that which a study of the geological deposits (and the fossils they contain) show to have been actually available. The discovery of the enormous, but gradually released disintegration energy of the radioactive elements enables us now to explain the prolonged period during which life has existed on the earth.

Exercises. — 1. Construct equations, showing the interactions of: (*a*) chromic oxide and aluminium, (*b*) strontium nitrate and potassium dichromate in solution, (*c*) potassium hydroxide and chromic hydroxide, and the reversal on boiling, (*d*) chlorine and potassium chromite in excess of alkali (what is the actual oxidizing agent?).

2. What volume of oxygen at 0° and 760 mm., (*a*) is obtainable from one formula-weight of potassium dichromate (par. 4, p. 599), (*b*) is required to oxidize one formula-weight of chromous chloride?

3. To what classes of actions should you assign the three methods of making chromic oxide (p. 603)?

4. Make equations for all the reactions involved in the preparation of sodium-diuranate from pitchblende.

5. How many candle power will be obtained from 50-watt carbon and tungsten filament lamps, respectively?

6. Point out the resemblance, and the differences between the reactions of, (*a*) gold with *aqua regia*, (*b*) calcium oxalate with hydrochloric acid, (*c*) barium chromate with nitric acid (p. 601).

CHAPTER XLIV

MANGANESE

The Chemical Relations of the Element. — Manganese stands, at present, alone on the left side of the eighth column of the periodic table. The right side is occupied by the halogens. It is never univalent, as are the halogens, but its heptoxide Mn_2O_7 and the corresponding acid, permanganic acid $HMnO_4$, are in many ways closely related to the heptoxide of chlorine and perchloric acid $HClO_4$. Of the lower oxides of manganese, MnO is basic, and Mn_2O_3 feebly basic. MnO_2 is feebly acidic, MnO_3 more strongly so, and permanganic acid (from Mn_2O_7) is a very active acid. Contrary to the habit of feebly acidic and feebly basic oxides, such as those of zinc, aluminium, and tin, the basic oxides of manganese are not at all acidic, and the acidic oxides, with the exception of MnO_2, are not also basic. There are thus the five following, rather well-defined sets of compounds, showing five different valences of the element. Of these the first, fourth, and fifth are the most stable and the most important.

1. **Manganous compounds,** MnO, $Mn(OH)_2$, $MnSO_4$, etc. These compounds resemble those of the magnesium family (and those of Fe^{++}). The salts of weak acids, such as the carbonate and sulphide, are easily made, and there is little hydrolysis of the halides. The salts are pale-pink in color.

2. **Manganic compounds,** Mn_2O_3, $Mn(OH)_3$, $Mn_2(SO_4)_3$, $[MnCl_3]$. The salts resemble the chromic and aluminium salts in behavior, but are even less stable than those of quadrivalent lead. They are completely hydrolyzed by little water. The salts are violet in color.

3. **Manganites,** MnO_2, H_2MnO_3, $CaMnO_3$. The alkali manganites are strongly hydrolyzed, like the plumbates and the stannates.

4. **Manganates,** MnO_3, H_2MnO_4, K_2MnO_4. The salts resemble the sulphates and chromates, but are much more easily hydrolyzed. The free acid resembles chloric acid (p. 314) in that, when it de-

composes, it yields a higher acid ($HMnO_4$) and a lower oxide (MnO_2). The salts are green in color.

5. **Permanganates,** Mn_2O_7, $HMnO_4$ (hydrated), $KMnO_4$. The salts resemble the perchlorates, and are not hydrolyzed by water. They are reddish-purple in color.

It will be seen that the element manganese changes its character totally with change in valence, and in each form of combination resembles some set of elements of valence identical with that which it has itself assumed. Since the valence represents the number of electrons gained or lost by each atom (p. 322), it is thus evident that the chemical properties of an element depend more upon the electrical constitution of its atom than upon the atomic weight. The latter is a secondary property, dependent on the former (*cf.* p. 304).

Occurrence: the Metal. — The chief ore is the dioxide, pyrolusite MnO_2, which always contains compounds of iron. Other manganese minerals are: braunite Mn_2O_3; the hydrated form, manganite $MnO(OH)$; hausmannite Mn_3O_4; and manganese spar $MnCO_3$. The metal is most easily made by reducing one of the oxides with aluminium by Goldschmidt's method.

The metal manganese (m.-p. 1260) has a grayish luster faintly tinged with red. It is oxidized superficially by air, and easily displaces hydrogen from dilute acids, giving manganous salts. Its alloys with iron, such as spiegel iron (5–15 per cent Mn) and ferromanganese (70–80 per cent Mn), are made by using manganese ores with the charge in the blast furnace, and are added to the iron in making special steels. **Manganese steel** (7–20 per cent Mn) is exceedingly hard, even when cooled slowly. It is used for the jaws of rock crushing machinery and for burglar-proof safes. Wire made of an alloy called **manganin** (Cu 84 per cent, Ni 4 per cent, Mn 12 per cent), invented by Weston, is used in instruments for making electrical measurements, because its resistance does not alter with moderate changes in temperature.

Oxides. — **Manganous oxide** MnO is a green powder, made by reducing any of the other oxides with hydrogen. **Hausmannite** Mn_3O_4 is dull red. An oxide having this composition is formed when any of the other oxides is heated in air, oxidation or reduction, as the case may be, taking place (*cf.* p. 575). **Manganic oxide** Mn_2O_3 is brownish-black, and is formed by heating any of the oxides in oxygen.

Manganese dioxide MnO_2 is black, and is most easily prepared in pure condition by gentle ignition of manganous nitrate. The hydrated forms of the oxide are produced by precipitation, as by adding a hypochlorite or hypobromite to manganous hydroxide suspended in water. Manganese dioxide is not a peroxide in the restricted sense (*cf.* p. 223). That is to say, it does not contain the radical O_2^{II} and, therefore, does not give hydrogen peroxide. Its reaction formula is $Mn(O)_2$ not $Mn(O_2)$ and in double decompositions it yields only water $H_2(O)$. It is used for manufacturing chlorine, although electrolytic processes are now driving it out of this field. In glass-making (*q.v.*), it is employed to oxidize the green ferrous silicate, derived from impurities in the sand, to the pale-yellow ferric compound. The amethyst color of the manganic silicate which is formed tends also to neutralize this yellow. It is mixed with black paints as a "dryer" (oxidizing agent).

Manganese trioxide MnO_3 is a red, unstable powder. **Manganese heptoxide** Mn_2O_7 is a brownish-green, volatile oil (see below).

When any of these oxides is heated with an *acid*, a manganous salt is obtained. Salts of this class are, in fact, the only stable substances in which manganese is combined with an acid radical. In this action the oxides containing more oxygen than does MnO give off oxygen, or oxidize the acid (*cf.* p. 157). When the oxides are heated with *bases*, in the presence of *air*, manganates are always formed. In this case, with oxides containing a smaller proportion of oxygen than MnO_3, oxygen is taken from the air.

Manganous Compounds. — The manganous salts are formed by the action of acids upon the carbonate or any of the oxides. Thus the **chloride** $MnCl_2,4H_2O$ is obtained in pale-pink crystals from a solution made by treating the dioxide with hydrochloric acid and driving off the chlorine liberated by oxidation (p. 158). The **hydroxide** $Mn(OH)_2$ is formed as a white precipitate when a soluble base is added to a solution of a manganous salt. This body passes into solution when ammonium salts are added, and cannot be precipitated in their presence on account of the formation of molecular ammonium hydroxide and the suppression of hydroxide-ion (*cf*. magnesium hydroxide, p. 525). The hydroxide quickly darkens when exposed to the air and passes over into hydrated manganic oxide $MnO(OH)$.

Manganous sulphate gives pink crystals of a hydrate. Below 6° the solution deposits $MnSO_4,7H_2O$, which is a vitriol (p. 529). Between 7° and 20° the product is $MnSO_4,5H_2O$, asymmetric and resembling $CuSO_4,5H_2O$. Above 25° monosymmetric prisms of $MnSO_4,4H_2O$ are obtained. These hydrates have different aqueous tensions and may be formed from one another by lowering or raising the pressure of water vapor around the substance (p. 96).

Manganous carbonate $MnCO_3$ is a white powder formed by precipitation. The **sulphide** MnS is obtained as a green, crystalline powder by leading hydrogen sulphide over any of the oxides. A flesh-colored, amorphous **manganous sulphide** MnS (often somewhat hydrated) is more familiar and is precipitated by ammonium sulphide from manganous salts. It interacts with mineral acids and even with acetic acid, so that it cannot be precipitated by the action of hydrogen sulphide on salts (*cf*. p. 530). When rubbed in a mortar it becomes crystalline, and is then green.

The manganous salts of weak acids, such as the carbonate and sulphide, darken when exposed to air and are oxidized, with formation of hydrated manganic oxide. As we have seen, manganous hydroxide is similarly oxidized and these salts are precisely the ones which should furnish the hydroxide by hydrolysis. While there is a general resemblance between the manganous salts and the stannous, chromous, and ferrous salts, the manganous salts of active acids are not oxidized by the air as are the corresponding salts of the other three metals.

Manganic Compounds. — The base of this set of compounds, **manganic hydroxide** $Mn(OH)_3$, is slowly deposited by the action of the air on an ammoniacal solution of a manganous salt in salts of ammonium. **Manganic chloride** $MnCl_3$ is present in the liquid obtained by the action of hydrochloric acid upon manganese dioxide (*cf*. p. 158), but loses chlorine very readily.

Manganites. — Although manganese dioxide interacts when fused with potassium hydroxide, simple salts derived from H_2MnO_3 $(= H_2O,MnO_2)$ or H_4MnO_4 $(= 2H_2O,MnO_2)$ are not formed. The products are complex, as $K_2Mn_5O_{11}$. Some less complex manganites are formed by mixing manganous chloride solution with slaked lime, and blowing air through the mass of calcium and manganous hydroxides which is thus obtained. Manganites of calcium, such as $CaMnO_3$ (= CaO,MnO_2) and $CaMn_2O_5$ (= $CaO,2MnO_2$) are thus formed:

$$Ca(OH)_2 + 2Mn(OH)_2 + O_2 \rightarrow CaMn_2O_5 + 3H_2O.$$

Manganates. — When one of the oxides of manganese is fused with potassium carbonate and potassium nitrate, a green mass is obtained. The green aqueous extract deposits **potassium manganate** K_2MnO_4 in rhombic crystals, which are of the same form as those of potassium sulphate, and are almost black:

$$K_2CO_3 + MnO_2 + O \rightarrow K_2MnO_4 + CO_2.$$

The acid H_2MnO_4 is itself unknown. The potassium salt remains unchanged in solution only in presence of free alkali. When the concentration of the hydroxide-ion is reduced by dilution, or, better still, when a weak acid such as carbonic acid or acetic acid is used to neutralize it, the salt is decomposed according to the following equation:

$$3K_2MnO_4 + 2H_2O \rightarrow 4KOH + 2KMnO_4 + MnO_2.$$

That is, a precipitate of manganese dioxide and a solution of potassium permanganate are obtained. To make the equation (pp. 322–324), we note that in K_2MnO_4 we have $2K^+$ and $4O^=$ and therefore Mn^{++++++} to secure electrical neutrality. The latter becomes $Mn^{+++++++}$ and Mn^{++++}. Arithmetically $3Mn^{++++++}$ will give $2Mn^{+++++++}$ and $1Mn^{++++}$. Hence, $3K_2MnO_4$ are required, and $2KMnO_4$ and $1MnO_2$ produced. In terms of the ions the equation is simpler:

$$3MnO_4^= + 2H^+ \rightarrow 2OH^- + 2MnO_4^- + MnO_2.$$

Permanganates. — **Potassium permanganate** $KMnO_4$ is made by decomposition of the manganate as shown above, and is obtained, in purple crystals with a greenish luster, by evaporation of the solution. To avoid the loss of manganese thrown down as dioxide, the action is carried out commercially by passing ozone through the solution of the manganate: $2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + O_2 + 2KOH$. **Sodium permanganate** $NaMnO_4$ is made in a similar manner. It is not obtainable in solid form, but its solution is known as "Condy's disinfecting fluid." This liquid owes its properties to the oxidizing power of the salt. **Permanganic acid** is a very active acid, that is, it is highly ionized in aqueous solution. A solid hydrate of the acid may be secured in reddish-brown crystals by adding sulphuric acid to a solution of barium permanganate and allowing the filtrate to evaporate:

$$Ba(MnO_4)_2 + H_2SO_4 + xH_2O \rightleftarrows BaSO_4 \downarrow + 2HMnO_4,xH_2O.$$

This hydrate decomposes, on being warmed to 32°, and yields oxygen and manganese dioxide. When a very little dry, powdered potassium permanganate is moistened with concentrated sulphuric acid, brownish-green, oily drops of **permanganic anhydride** (manganese heptoxide) Mn_2O_7 are formed. This compound is volatile, giving a violet vapor, and is apt to decompose explosively into oxygen and manganese dioxide. Its oxidizing power is such that combustibles like paper, ether, and illuminating gas are set on fire by contact with it.

Potassium Permanganate as an Oxidizing Agent. — The actions are different according as the substance is employed (1) in acid, or (2) in neutral solution.

1. In presence of an acid, and an oxidizable body, a manganous salt is always formed. The schematic equation, $Mn_2O_7 \rightarrow 2MnO + 5O$, shows that every two molecules of the permanganate yield 5O for oxidizing purposes. Thus, when sulphuric acid is added to potassium permanganate solution, and sulphur dioxide is led through the mixture, we have:

$$\begin{array}{rr} 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O (+5O) & (1) \\ (5O) + 5H_2SO_3 \rightarrow 5H_2SO_4 & (2) \\ \hline 2KMnO_4 + 3H_2SO_4 + 5H_2SO_3 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5H_2SO_4 & \end{array}$$

In this case, since sulphuric acid is a product, the preliminary addition of the acid was superfluous. In other cases, the partial equation (1), showing the available 5O, remains the same, while the other partial equation varies with the substance being oxidized. Thus, with hydrogen sulphide as reducing agent, we have:

$$(O) + H_2S \rightarrow H_2O + S \qquad \times 5 \qquad (2')$$

and with ferrous sulphate, we get ferric sulphate:

$$2FeSO_4 + H_2SO_4(+ O) \rightarrow Fe_2(SO_4)_3 + H_2O \qquad \times 5 \qquad (2'')$$

As before (2′) and (2″) must be multiplied throughout by five, before summation is made (see also p. 225).

The quantity of a ferrous salt, or of hydrogen peroxide (p. 225) in a sample of a solution may be measured by titrating (p. 257) the solution with a standard solution of potassium permanganate until the color ceases to be destroyed, and then noting the volume used. For iron, the standard solution may be prepared so that 1 cc. will oxidize 0.01 g. of Fe^{++}.

2. When dry potassium permanganate is heated, it decomposes as follows:

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2.$$

The neutral solution oxidizes substances which are reducing agents. The fingers are stained brown by an aqueous solution, receiving a deposit of manganese dioxide, in consequence of the reducing power of the unstable organic substances in the skin. The destruction of minute organisms by Condy's fluid results from a similar action. When the powdered salt is moistened with glycerine, the mass presently bursts into flame.

Analytical Reactions of Manganese Compounds. — The ions commonly encountered are manganous-ion Mn^{++}, which is very pale-pink in color, permanganate-ion MnO_4^-, which is purple, and manganate-ion $MnO_4^=$, which is green. The manganous compounds give with ammonium sulphide the flesh-colored sulphide which is soluble in acids. Bases give the white hydroxide, which darkens by oxidation, and is soluble in salts of ammonium. All compounds of manganese confer upon the borax bead an amethyst color (manganic borate), which, in the reducing flame, disappears (manganous borate). A bead of sodium carbonate and niter becomes green on account of the formation of the manganate.

Exercises. — 1. What do we mean by saying that, (*a*) chromous chloride is stable (p. 93), but easily oxidized by the air, (*b*) permanganic acid is an active oxidizing agent in presence of an acid (p. 622).

2. Formulate the oxidations of hydrogen sulphide, of ferrous sulphate, of oxalic acid (to carbon dioxide), and of nitrous acid (to nitric acid) by potassium permanganate in acid solution. In doing so, employ the several methods suggested on pp. 322–326.

CHAPTER XLV

IRON, COBALT, NICKEL

THE elements **iron** (Fe, at. wt. 55.84), **cobalt** (Co, at. wt. 59), and **nickel** (Ni, at. wt. 58.7) are not corresponding members of successive periods, like the families hitherto considered. They are neighboring members of the first long period, lying between its first and second octaves.

IRON Fe

Chemical Relations of the Element. — The oxides and hydroxides FeO and $Fe(OH)_2$, Fe_2O_3 and $Fe(OH)_3$ are basic, the former more strongly so than the latter. The ferrous salts, derived from $Fe(OH)_2$, resemble those of the magnesium group and those of Cr^{++} and Mn^{++}, and are little hydrolyzed. The ferric salts, derived from $Fe(OH)_3$, resemble those of Cr^{+++} and Al^{+++} and are hydrolyzed to a considerable extent. Iron gives also a few **ferrates** K_2FeO_4, $CaFeO_4$, etc., derived from an acid H_2FeO_4 which, like manganic acid H_2MnO_4 (p. 621), is too unstable to be isolated. Complex anions containing iron, such as the anion of $K_4.Fe(CN)_6$, are familiar, but complex cations containing ammonia are unknown.

Occurrence. — Free iron is found in minute particles in some basalts, and many meteorites are composed of it. Meteoric iron can be distinguished from specimens of terrestrial origin by the fact that it contains 3–8 per cent of nickel. The chief ores of iron are the oxides, hæmatite Fe_2O_3 and magnetite Fe_3O_4, and the carbonate $FeCO_3$, siderite. The first is reddish and radiated in structure; but black, shining, rhombohedral crystals, known as specularite, are also found. Hydrated forms, like brown iron ore $2Fe_2O_3,3H_2O$, are also common. Siderite is pale-brown in color and rhombohedral, like calcite. When mixed with clay it forms iron-stone, from which most of the iron in Great Britain, but less than one per cent of that in the United States is obtained. Pyrite

FeS_2 consists of golden-yellow, shining cubes or pentagonal dodecahedra. It is used, on account of its sulphur, in the manufacture of sulphuric acid, but, from the oxidized residue, iron of sufficient purity is obtained with difficulty. Compounds of iron are contained in chlorophyll and in the blood (hæmoglobin), and doubtless play an important part in connection with the vital functions of these substances. Ammonium sulphide blackens the skin, forming ferrous sulphide by interaction with organic compounds of iron present in the tissues.

Pure Iron. — Pure iron is obtained by reducing pure ferrous oxalate in a stream of hydrogen at a high temperature. It is also made by electrolysis of ferrous sulphate solution at 100° between iron electrodes. It is silver-white and melts at 1510°. The purest iron does not rust in pure cold water, but the impurities in ordinary iron act as contact agents and rusting proceeds.

Metallurgy. — The ores of iron are first roasted in order to decompose carbonates and oxidize sulphides, if these salts are present. Coke is then used to reduce the oxides. Coal is unsuitable because so much heat is wasted in driving out the volatile matter and moisture, which are absent from coke. Ores containing lime or magnesia are mixed with an acid flux, such as sand or clay-slate, in order that a fusible slag may be formed. Conversely, ores containing silica and clay are mixed with limestone. With proper adjustment of the ingredients the process can be carried on *continuously* in a **blast furnace** (Fig. 136), an iron structure 40 to 100 feet high, lined with firebrick. The solid materials thrown in at the top are converted, as they slowly descend, completely into gases which escape and liquids (iron and slag) which are tapped off at the bottom. Heated air is blown in at the bottom through tuyères, and the top is closed by a cone which descends for a moment when an addition is made to the charge. The gases, which contain much carbon monoxide, are led off and used to heat the blast or to drive gas-engines.

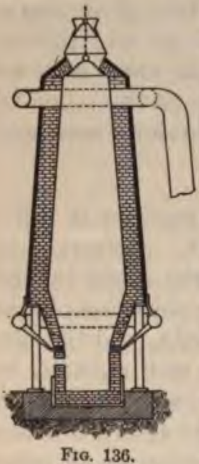


FIG. 136.

The main action takes place between the carbon monoxide, present in consequence of the excess of carbon, and the oxide of iron:

$$Fe_3O_4 + 4CO \rightleftarrows 3Fe + 4CO_2.$$

Since the action is a reversible one, a large excess of carbon monoxide is required. At 650°, equilibrium is reached with $CO : CO_2 ::$ 1 vol. : 1½ vols., and in practice the proportion of carbon monoxide used is from twice to fifteen times as great. Almost 5 tons of air, heated in advance to 800°, are required for each ton of iron produced. The moisture in this air acts upon the coke, giving water-gas (p. 386). This action uses up fuel, and also lowers the temperature at the point where it should be highest. In the most modern furnaces, therefore, the air is dried (Gayley dry-blast process), with a saving in coke equivalent to $1.00 (4/–) per ton of iron obtained. This illustrates the commercial value of even a single improvement in a chemical operation. If the Gayley process were used with every blast furnace, an immense sum would be saved, for in the United States alone 30 million tons of iron are annually produced (1913). This is considerably over 40 per cent of the world's production, 20 per cent being supplied by Germany and 15 per cent by Great Britain.

In the upper part of the furnace, the heat (400°) loosens the texture of the ore. Further down, the temperature is higher (500–900°), and the carbon monoxide reduces the oxide of iron to particles of soft iron. A temperature high enough to melt pure iron is barely reached anywhere in the furnace, but, a little lower down, by solution of carbon in the iron, the more fusible cast iron (m.-p. about 1200°) is formed and falls in drops to the bottom. It is in this region also that the slag, essentially a glass (p. 493), is produced. If the flux had begun sooner to interact with the unreduced ore, iron would have been lost by the formation of the silicate. The iron collects below the slag, and the latter flows continuously from a small hole. The former is tapped off at intervals of six hours or so from a lower opening. As a rule, the iron never cools until it has been converted into rails or structural iron. In some cases, it is made into "pigs" in a casting machine.

Cast Iron and Wrought Iron. — Pure iron is not manufactured, and indeed would be too soft for most purposes. Pianowire, however, is about 99.7 per cent pure. The product obtained from the blast furnace contains 92–94 per cent of iron along with 2.6–4.3 per cent of carbon, often nearly as much silicon, varying proportions of manganese, and some phosphorus and sulphur. The last four ingredients are liberated from combination with oxygen by the carbon in the hottest part of the furnace and combine or alloy themselves with the iron. Cast iron does not soften before melting, as does the purer wrought iron (m.-p. 1510°), but melts sharply at 1150–1250° according to the amount of foreign material it contains. When *suddenly* cooled it gives **chilled cast iron** which is very brittle and looks homogeneous to the eye, all the carbon being present in the form of carbide of iron Fe_3C (cementite) in solid solution in the metal. This solid solution is exceedingly hard, but very brittle. By slower cooling, time is permitted for the separation of part of the carbon as graphite, which appears in tiny black scales, and **gray cast iron** results. This mixture is much softer, on account of the amount of free, relatively pure iron which it contains.

Cast iron is **used** in making cooking ranges, stoves, pipes, and radiators. It expands in solidifying, and so fills every detail of the mold.

Wrought iron, invented by Henry Cort (1784), is made by heating the broken pigs of cast iron upon a layer of material containing oxide of iron and hammer-slag (basic silicate of iron) spread on the bed of a reverberatory furnace (Fig. 116, p. 460). The carbon, silicon, and phosphorus combine with the oxygen of the oxide, and the last two pass into the slag. The sulphur is found in the slag as ferrous sulphide. On account of the effervescence due to the escape of carbon monoxide, the process is called "pig-boiling." The iron is stirred with iron rods ("puddled") and stiffens as it becomes purer, until finally it can be withdrawn in balls ("blooms") and partially freed from slag by rolling. The resulting bars are repeatedly cut, piled in a bundle, reheated, and rolled. The iron now softens sufficiently for welding below 1000° and melts at 1505°. Its fibrous structure is due partly to the films of slag which have not been completely pressed out by the rolling. On account of its toughness, wrought iron is **used** for anchors, chains, and bolts, and for drawing into wire. On account of its relative purity (99.8–99.9 per cent), it is less fusible than cast iron and is used for fire bars. The above operations are now largely performed by machinery, but have been largely displaced by the Bessemer and open hearth processes in which iron of equal purity can be obtained.

Properties of Steel. — This is a variety of iron almost free from phosphorus, sulphur, and silicon. Tool-steel contains 0.9–1.5 per cent of carbon, structural steel only 0.2–0.6 per cent, and mild steel 0.2 per cent or even less. Steel combines the properties of cast and of wrought iron, being hard and elastic, and at the same time available for forging and welding when the proportion of carbon is not too high. Steel can be tempered (see below). It has also a greater tensile strength* than has wrought iron, and it can be permanently magnetized.

Bessemer Process. — Steel is made largely by the Bessemer process (Kelly 1852, Bessemer 1855). The molten cast iron is poured into a converter (Fig. 137) and a blast of air (*a*) is blown through it. The oxidation of the manganese, carbon, silicon, and a little of the iron gives out sufficient heat to raise the temperature of the mass above the melting-point of wrought iron. The required proportion of carbon is then introduced by adding pure cast iron, spiegel iron, or coke, and the contents, first the slag, and then the molten steel, are finally poured out by turning the converter. When the cast iron contains much phosphorus, the oxide of this element is reduced again by the iron as fast as it is formed by the blast. In such cases a basic lining containing lime and magnesia takes the place of the sand and clay lining of the ordinary Bessemer converter, and a slag containing a basic phosphate of calcium is produced. This modification constitutes what is known as the basic or Thomas-Gilchrist process. The slag ("Thomas-slag") when pulverized forms a valuable fertilizer

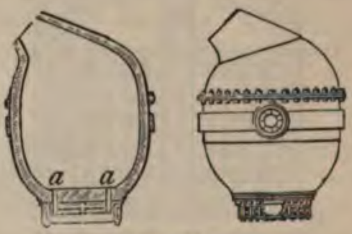


Fig. 137.

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* **Tensile strength** or **tenacity** is measured by the weight (in kilos) required to break a wire of the metal 1 sq. mm. in section. Lead 2.6, copper 51, iron 71, steel 91.

(*cf.* p. 488). In the United States, the basic open-hearth process is preferred.

Open-Hearth (*Siemens-Martin*) ***Process.***—In this process the cast iron is melted in a saucer-shaped depression (Fig. 138), which is lined with sand in the acid process and with lime and magnesia in the basic process. Scraps of iron plate (for dilution) and hæmatite, or some other oxide ore, are then added in proper proportions. The materials (50–75 tons in one charge) are heated with gas fuel for 8–10 hours. To secure economically the high temperature required to keep the product (almost pure iron) fused, Siemens devised the method of preheating the fuel gas and air by a regenerative device. The spent air and gas pass down through a checkerwork of brick. When this becomes heated, the valves are reversed, the gas and air now enter through the heated brickwork and, after meeting and burning over the iron, pass out through the checkerwork on the opposite side, raising its temperature in turn.

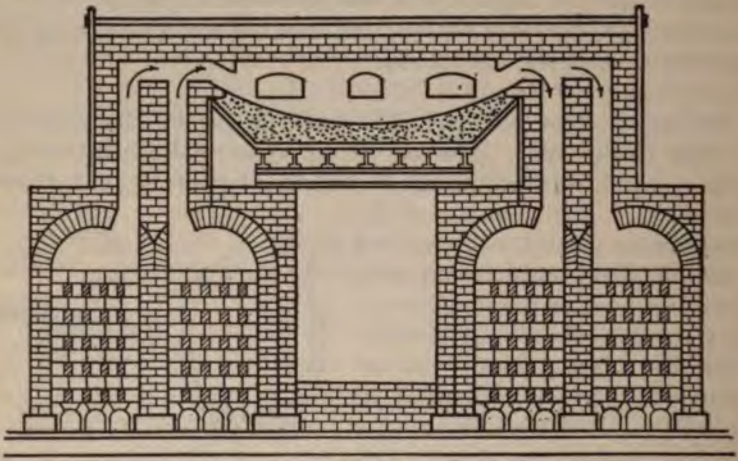

FIG. 138.

The changes are similar to those in the Bessemer process. During casting, some aluminium is added to combine with oxygen (present as CO) and give sounder ingots. Recently, iron containing 10–15 per cent of titanium has been added instead. The titanium combines with both nitrogen and oxygen and the compounds pass into the slag, just as does aluminium oxide. Rails made of steel purified with this element are less liable to breakage (the commonest cause of wrecks) and are 40 per cent more durable, than are ordinary open-hearth rails.

The advantage of the open-hearth process over that of Bessemer is that it is not hurried, and is therefore under better control. The material can be tested by sample at intervals until the required composition has been reached. The product is of more uniform quality. When fine steel is required, electric heating (*e.g.*, in the Héroult furnace) permits even more deliberate treatment.

Bessemer and open-hearth steel is used for heavy and light machinery castings and for shafts. It is rolled into rails, and into bridge and structural iron.

Crucible Steel. — For special purposes steel is made in crucibles of clay (or graphite and clay) in melts of 60–100 pounds. "Melting bar," a very pure open-hearth steel, is melted with charcoal or with pure pig iron. This steel is employed in making razors (1.5 per cent C), tools (1 per cent C), dies (0.75 per cent C), pens, needles, and cutlery.

Tempering. — The carbon in steel (and cast iron) is in the form of carbon or of carbide of iron Fe_3C (6.6 per cent C), dissolved in the iron. When white hot steel (up to 2 per cent C) is suddenly chilled, there is no time for any changes to occur during the cooling, and a *solid solution* is obtained which is very hard and brittle. When, however, the cooling is slow, some of the carbon separates in minute crystals of cementite Fe_3C until, at about 700°, there remains only about 0.9 per cent carbon in solid solution. At this temperature, if sufficient time is allowed, the solid solution separates into a mixture of pure iron (87 per cent) which is soft and carbide of iron (13 per cent) which is hard. Steel, when slowly cooled, is thus a mixture, and not homogeneous. If, therefore, hard chilled steel is heated once more for the purpose of tempering, the extent to which the softer material is formed depends upon the temperature reached and upon the rate and the duration of the cooling process. By varying these, the degree of hardness allowed to remain can be adjusted.

Steel Alloys. — As we have seen, substances such as aluminium, titanium, and ferrosilicon are added to iron for the purpose of purifying it, and pass in combination into the slag. There are, however, regular alloys containing the foreign metal along with the iron. Thus, **manganese steel** (7–20 per cent Mn), made by adding spiegel iron or ferromanganese (p. 618) to steel, remains hard even when cooled slowly and is used for the jaws of rock-crushers and for safes. **Chromium-vanadium steel** (1 per cent Cr, 0.15 per cent Va) has great tensile strength, can be bent double while cold, and offers great resistance to changes of stress and to torsion. It is used for frames and axles of automobiles and for connecting rods. **Tungsten steel** has already been described (p. 606). **Nickel steel** (2–4 per cent Ni) resists corrosion, has a high limit of elasticity and great hardness, and is used for armor-plate, wire cables, and propeller shafts. **Invar** (36 per cent Ni) is practically non-expansive when heated within narrow limits and is used for meter-scales and pendulum rods.

Chemical Properties of Iron. — Although the purest iron does not rust in cold water (p. 626), ordinary iron rusts in moist air or under water. It probably rusts in water free from carbon dioxide, displacing the hydrogen-ion, but the action is greatly hastened by the presence of carbonic acid. Rust is a brittle, porous, loosely adherent coating of variable composition, consisting mainly of a hydrated ferric oxide $3Fe_2O_3,H_2O$, which does not protect the metal below. Oil protects iron from rusting because, although oxygen is more soluble in most oils than in water, and so reaches the iron freely, water is not soluble in oil and so moisture is excluded.

Iron burns in oxygen and it interacts with superheated steam, in both cases giving Fe_3O_4. A superficial layer of this oxide adheres firmly and protects the iron from the action of the air (Barff's process iron, or Russia iron).

Iron displaces hydrogen easily from dilute acids. Steel and cast iron, which contain iron, its carbide, and graphite, give with cold dilute acids almost pure hydrogen, and the carbide and graphite remain unattacked. More concentrated acids, however, particularly when warm, generate, along with hydrogen, hydrocarbons formed by interaction with the carbide (p. 441). The odor of the gas is due to compounds of sulphur and phosphorus.

Although iron acts vigorously on dilute or concentrated nitric acid, it is indifferent to fuming nitric acid (NO_2 in solution, p. 348). It becomes **passive**. In this state, it no longer displaces hydrogen from dilute acids. If dipped in cupric sulphate solution, it does not receive the usual red coating of metallic copper. However, if scratched or struck, the passive condition is destroyed, and copper begins to be deposited at the point touched and the action spreads quickly over the whole surface. No satisfactory explanation of this phenomenon has been obtained, although it is shown also by chromium, cobalt, and other metals.

Ferrous Compounds. — **Ferrous chloride** is obtained as a pale-blue hydrate $FeCl_2,4H_2O$ (turning green in the air) by interaction of hydrochloric acid with the metal or the carbonate. The anhydrous salt sublimes in colorless crystals when hydrogen chloride is led over the heated metal. In solution the salt is oxidized by the air to a basic ferric chloride:

$$4Fe^{++} + O_2 + 2H_2O \rightarrow 4Fe^{+++} + 4OH^-.$$

In presence of excess of the acid, normal ferric choride is formed. With nitric acid, ferric chloride and nitric oxide are produced (p. 350).

Ferrous hydroxide $Fe(OH)_2$ is thrown down as a white precipitate, but rapidly becomes dirty-green and finally brown, by oxidation. It dissolves in solutions of salts of ammonium, being like magnesium hydroxide (p. 525), sufficiently soluble in water to require an appreciable concentration of OH^- for its precipitation. The NH_4^+ from the salts combines with the OH^- formed by the ferrous hydroxide to give molecular ammonium hydroxide. **Ferrous oxide** FeO is black, and is formed by heating ferrous oxalate in absence of air. It is made also by cautious reduction of ferric oxide by hydrogen (at about 300°), but is easily reduced further to the metal. It catches fire spontaneously when exposed to the air.

Ferrous carbonate $FeCO_3$ is found in nature as siderite, and may be made in slightly hydrolyzed form by precipitation. The precipitate is white but rapidly darkens and finally becomes brown, the ferrous hydroxide produced by hydrolysis being oxidized to the ferric condition. The salt interacts with water containing carbonic acid, after the manner of calcium carbonate (p. 383), giving $FeH_2(CO_3)_2$, and hence is found in solution in natural (chalybeate) waters.

Ferrous sulphide FeS may be formed as a black, metallic-looking mass by heating together the free elements. It is produced by precipitation with ammonium sulphide, but not with hydrogen sulphide. It interacts readily with dilute acids. The precipitated form is slowly oxidized to ferrous sulphate by the air.

Ferrous sulphate is obtained by allowing pyrites to oxidize in the air and leaching the residue:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4.$$

The liquor is treated with scrap iron and the neutral solution evaporated until a hydrate $FeSO_4,7H_2O$, green vitriol, or "copperas," is deposited. The crystals are efflorescent, and become also brown from oxidation to a basic ferric sulphate:

$$4FeSO_4 + O_2 + 2H_2O \rightarrow 4Fe(OH)SO_4.$$

With excess of sulphuric acid and air, or an oxidizing agent such as nitric acid, ferric sulphate is formed. The ferrous sulphate is **used** in dyeing and in making **writing-ink.** The extract of nut-galls contains tannic acid, $HC_{14}H_9O_9$, which, with ferrous sulphate, gives ferrous tannate, a soluble, almost colorless salt. A solution of this salt containing gum-arabic and some blue or black dye constitutes the ink. When the writing is exposed to the air, the ferrous tannate is oxidized to the ferric condition, and the ferric compound is a fine, black precipitate (*cf.* p. 516). The dye is added to make the writing visible from the first. Ferrous sulphate is also used in the purification of water (p. 560).

Ferric Compounds. — By leading chlorine into a solution of ferrous chloride, and evaporating until the proper proportion of water alone remains, a yellow, deliquescent **hexahydrate** of **ferric chloride,** $FeCl_3,6H_2O$ is obtained. When this is heated still further, hydrolysis takes place and the oxide remains. When chlorine is passed over heated iron, **anhydrous** ferric chloride sublimes in dark green scales, which are red by transmitted light. In solution, the salt, like other ferric salts, can be reduced to the ferrous condition by boiling with iron. The same reduction is effected by hydrogen sulphide:

$$2Fe^{+++} + Fe \rightarrow 3Fe^{++}.$$
$$2Fe^{+++} + S^{=} \rightarrow 2Fe^{++} + S\downarrow.$$

The ferric ion is almost colorless, the yellow-brown color of solutions of ferric chloride being due to the presence of ferric hydroxide produced by hydrolysis. The color deepens when the solution is heated (increased hydrolysis), and fades again very slowly, by reversal of the action, when the cold solution is allowed to stand.

Ferric hydroxide $Fe(OH)_3$ appears as a brown precipitate when a base is added to a ferric salt. It does not interact with excess of the alkali. In this form the substance dries to the oxide without giving definite intermediate hydrated oxides. The hydrates, $Fe_2O_3,2Fe(OH)_3$ (brown iron ore) and $Fe_2O_3,4Fe(OH)_3$ (bog iron ore), however, are found in nature (see Rust, p. 632). The hydroxide passes easily into colloidal solution in a solution of ferric chloride, and by subsequent dialysis through a piece of parchment the salt can be separated, and a pure colloidal suspension of the hydroxide obtained. This suspension, known as **dialyzed iron,** is red in color, shows no depression in the freezing-point, and is not an electrolyte. The hydroxide is a positive colloid and is coagulated (brown precipitate) by the addition of salts, bivalent negative ions being more effective than univalent ones (p. 417).

Ferric oxide, Fe_2O_3, is sold as "rouge" and "Venetian red." It is made from the ferrous sulphate, obtained in cleaning iron ware which is to be tinned or galvanized, and in other ways in the arts. The salt is allowed to oxidize, and the ferric hydroxide, thrown down by the addition of lime, is calcined. The product varies in tint from a bright yellowish-red to a dark violet-brown according to the fineness of the powder. The best rouge is obtained by calcining ferrous oxalate FeC_2O_4. This oxide is not distinctly acidic, but by fusion with more basic oxides, compounds like franklinite $Zn(FeO_2)_2$ may be formed. It is reduced by hydrogen, at about 300° to ferrous oxide, and at 700–800° to metallic iron.

Magnetic oxide of iron Fe_3O_4 or lodestone is found in nature, and is formed by the action of air (hammer-scale), steam, or carbon dioxide on iron. It forms octahedral crystals, and is a ferrous-ferric oxide FeO,Fe_2O_3 or $Fe(FeO_2)_2$, related to franklinite.

Ferric sulphide Fe_2S_3 may be made by fusing together the free elements, and is obtained also as a precipitate by the addition of ammonium sulphide to ferric chloride solution (Stokes). With hydrogen sulphide, only sulphur is thrown down (p. 635).

Ferric sulphate $Fe_2(SO_4)_3$ is formed by oxidation of ferrous sulphate, and is obtained as a white mass by evaporation. It gives alums (p. 558), such as ferric-ammonium alum $(NH_4)_2SO_4,Fe_2(SO_4)_3,24H_2O$, which are almost colorless when pure, but usually have a pale reddish-violet tinge.

Pyrite. — The mineral pyrite FeS_2 (Fools' gold) is the sulphide of iron which is most stable in the air. It is found in nature in the form of glittering, golden-yellow cubes, octahedrons, and pentagonal dodecahedrons. It is not attacked by dilute acids, but concentrated hydrochloric acid slowly converts it into ferrous chloride and sulphur. It is reduced by hydrogen to ferrous sulphide.

Cyanides. — When potassium cyanide is added to solutions of ferrous or ferric salts, yellowish precipitates are produced, but the simple cyanides cannot be obtained in pure form. These precipitates interact with excess of the cyanide giving soluble complex cyanides of the forms $4KCN,Fe(CN)_2$ and $3KCN,Fe(CN)_3$. These are called ferro- and ferricyanide of potassium, respectively.

Ferrocyanide of potassium $K_4Fe(CN)_6,3H_2O$, "yellow prussiate of potash," is made by heating nitrogenous animal refuse, such as blood, with iron filings and potassium carbonate. The resulting mass contains potassium cyanide and ferrous sulphide, and when it is treated with warm water these interact and produce the ferrocyanide:

$$2KCN + FeS \rightarrow Fe(CN)_2 + K_2S,$$
$$4KCN + Fe(CN)_2 \rightarrow K_4.Fe(CN)_6.$$

The salt is made also from the cyanogen contained in crude illuminating gas. The trihydrate forms large, yellow, monosymmetric tables. The solution contains almost exclusively the ions K^+ and $Fe(CN)_6^{==}$, and gives none of the reactions of the ferrous ion Fe^{++}. The corresponding acid $H_4.Fe(CN)_6$ may be obtained as white crystalline scales by addition of an acid and of ether (in which the substance is less soluble than in water) to the salt. The acid is a fairly active one, but is unstable and decomposes in a complex manner. Other ferrocyanides may be made by precipitation. That of copper $Cu_2.Fe(CN)_6$ is brown, and ferric ferrocyanide $Fe_4[Fe(CN)_6]_3$ has a brilliant blue color (**Prussian blue**). The ferrous compound (insoluble) $Fe_2Fe(CN)_6$, or perhaps $K_2FeFe(CN)_6$, is white but quickly becomes blue by oxidation. The soluble ferrocyanides are *not* poisonous.

Ferricyanide of potassium $K_3Fe(CN)_6$ is easily made from the ferrocyanide by oxidation:

$$2K_4Fe(CN)_6 + Cl_2 \rightarrow 2KCl + 2K_3.Fe(CN)_6,$$

or

$$2Fe(CN)_6^{==} + Cl_2 \rightarrow 2Fe(CN)_6^{=-} + 2Cl^-.$$

It forms red monosymmetric prisms. The free acid $H_3Fe(CN)_6$ is unstable. Other salts may be prepared by precipitation. Ferrous ferricyanide $Fe_3[Fe(CN_6)]_2$ is deep-blue in color (**Turnbull's blue**). With ferric salts only a brown solution is obtained.

Prussian blue and Turnbull's blue are **used** in making laundry blueing. They are insoluble, but give colloidal suspensions and are adsorbed by the material of the cloth.

Blue-Prints. — Some ferric salts, when exposed to light, are reduced to the ferrous condition. Thus, ferric oxalate, in the light, gives ferrous oxalate:

$$Fe_2(C_2O_4)_3 \rightarrow 2FeC_2O_4 + 2CO_2.$$

When paper is coated with ferric oxalate solution and dried, and an ink drawing on transparent paper is placed over the prepared surface, sunlight will reduce the iron to the ferrous condition, excepting where the ink protects it. When the sheet is then dipped in potassium ferricyanide solution (developer), the ferric oxalate gives only the brown substance which can be washed out. But the deep blue, insoluble ferrous ferricyanide is precipitated in the pores of the paper where the light has acted. The drawing appears white on a blue background. In ordinary blue-print paper, ammonium-ferric citrate takes the place of the oxalate, and the ferricyanide has already been applied to the paper before drying, so that only exposure and washing remain to be done. Dilute sodium hydroxide solution decomposes the ferricyanide, and is used for writing (in white) on blue-prints.

Iron Carbonyls. — When carbon monoxide is led over finely divided iron at 40–80°, or under eight atmospheres pressure at the ordinary temperature, volatile compounds of the composition $Fe(CO)_4$, **iron tetracarbonyl,** and $Fe(CO)_5$, the **pentacarbonyl,** are formed. When the gaseous mixture is heated more strongly, the compounds decompose again, and iron is deposited. Illuminating-gas burners frequently receive a deposit of iron from this cause.

Analytical Reactions of Compounds of Iron. — There are two ionic forms of iron, ferrous-ion Fe^{++}, which is very pale-green, and ferric-ion Fe^{+++}, which is almost colorless. Ammonium sulphide gives with the former black ferrous sulphide, which is soluble in dilute acids. The hydroxides are white and brown, respectively, and ferrous carbonate is white. With ferric salts, which are hydrolyzed (about 5%), carbonates yield the hydroxide because they neutralize the free acid and displace the equilibrium. With ferrocyanide of potassium, ferrous salts give a white, and ferric salts a blue precipitate. With ferricyanide of potassium the former gives a deep-blue precipitate, and the latter a brown solution. **Ferric thiocyanate** $Fe(CNS)_3$ is deep-red (p. 182). With borax, iron compounds give a bead which is green (ferrous borate) in the reducing flame, and colorless or, with much iron, yellow (ferric borate) or even brown when oxidized.

COBALT Co

The Chemical Relations of the Element. — Cobalt forms cobaltous and cobaltic oxides and hydroxides CoO and $Co(OH)_2$, Co_2O_3 and $Co(OH)_3$, respectively, which are all basic, the former, more so than the latter. The cobaltous salts are little hydrolyzed, but the cobaltic salts are largely decomposed by water. The latter also liberate readily one-third of the negative radical, after the manner of manganic salts, becoming cobaltous. Complex cations and anions containing cobalt are very numerous and very stable.

Occurrence and Properties. — Cobalt is found along with nickel in smaltite $CoAs_2$ and cobaltite $CoAsS$. The pure metal may be made by Goldschmidt's process, or by reducing the oxalate, or an oxide, with hydrogen.

The metal is silver-white, with a faint suggestion of pink. It is markedly crystalline, less tough than iron, and has no commercial applications. It displaces hydrogen slowly from dilute acids, but interacts readily with nitric acid.

Cobaltous Compounds. — The **chloride** $CoCl_2,6H_2O$ may be made by treating the oxide with hydrochloric acid. It forms red prisms, and when partially or completely dehydrated becomes deep-blue. Writing made with a diluted solution upon paper is almost invisible, but becomes blue when warmed and afterwards takes up moisture from the breath, and is once more invisible (**sympathetic ink**). Most cobaltous compounds are red when hydrated or in solution (Co^{++}), and blue when dehydrated. By addition of sodium hydroxide to a cobaltous salt, a blue basic salt is precipitated. When the mixture is boiled, the pink **cobaltous hydroxide** $Co(OH)_2$ is formed. This becomes brown through oxidation by the air. It interacts with ammonium hydroxide, giving a soluble ammonio-cobaltous hydroxide, which is quickly oxidized by the air to an ammonio-cobaltic compound (see below). It dissolves also in salts of ammonium as does magnesium hydroxide (p. 525). When dehydrated it leaves the black **cobaltous oxide** CoO. **Cobaltous sulphate,** $CoSO_4,7H_2O$, and **cobaltous nitrate,** $Co(NO_3)_2,6H_2O$, are familiar salts. The black **cobaltous sulphide** CoS is precipitated by ammonium sulphide from solutions of all salts, and even by hydrogen sulphide from the acetate, or a solution containing much sodium acetate (*cf.* p. 484). Once it has been formed, it interacts very slowly even with dilute hydrochloric acid, having apparently changed into a less active form. A sort of **cobalt glass,** made by fusing sand, cobalt oxide, and potassium nitrate, forms, when powdered, a blue pigment, **smalt,** used in china-painting and by artists.

Cobaltic Compounds. — By addition of a hypochlorite to a solution of a cobaltous salt, **cobaltic hydroxide** $Co(OH)_3$, a black powder, is precipitated. Cautious ignition of the nitrate gives **cobaltic oxide** Co_2O_3. Stronger ignition gives the commercial oxide, which is a **cobalto-cobaltic oxide** Co_3O_4. Cobaltic oxide dissolves in cold hydrochloric acid, but the solution gives off chlorine when warmed. By placing cobaltous sulphate solution round the anode of an electrolytic cell, crystals of **cobaltic sulphate,** $Co_2(SO_4)_3$, have been made and cobaltic alums have also been prepared (Hugh Marshall).

Complex Compounds. — Potassium cyanide precipitates from cobaltous salts a brownish-white cyanide. This interacts with excess of the reagent, giving a solution of **potassium cobaltocyanide** $K_4.Co(CN)_6$ (*cf.* p. 636). This compound is easily oxidized by chlorine, or even when the solution is boiled in the air, and the colorless **potassium cobalticyanide** is formed:

$$4K_4Co(CN)_6 + 2H_2O + O_2 \rightarrow 4K_3.Co(CN)_6 + 4KOH.$$

The solution gives none of the reactions of Co^{+++}, and with acids the very stable cobalticyanic acid, $H_3Co(CN)_3$, is liberated.

When acetic acid and potassium nitrite are added to a cobaltous salt, the latter is oxidized by the nitrous acid (liberated by the acetic acid) and a white complex salt $K_3.Co(NO_2)_6,nH_2O$ (= $Co(NO_2)_3,3KNO_2$), **potassium cobaltinitrite,** is thrown down.

Cobaltic salts give with ammonia complex compounds which are many and various. The cations often contain negative groups, and are such as $Co(NH_3)_6^{+++}$, $Co(NH_3)_5Cl^{++}$ and $Co(NH_3)_5NO_2^{++}$. Usually the solutions give none of the reactions of cobaltic ions, and often fail likewise to give those of the anion of the original salt.

NICKEL Ni

The Chemical Relations of the Element. — Nickel forms nickelous and nickelic oxides and hydroxides NiO and $Ni(OH)_2$, Ni_2O_3, and $Ni(OH)_3$, but only the former are basic. The nickelous salts resemble the cobaltous and ferrous salts, but are not oxidizable into corresponding nickelic compounds. Since there are no nickelic salts, there are here no analogues of the cobalticyanides or the cobaltinitrites. The complex nickelous salts, like the complex cobaltous salts, and unlike the complex cobaltic salts, are unstable, and so give some of the reactions of Ni^{++}.

Occurrence and Properties. — Nickel occurs free in meteorites and in niccolite NiAs and nickel glance NiAsS. It is now manufactured chiefly from pentlandite [Ni,Cu,Fe]S and other minerals found at Sudbury (Ontario), and from garnierite, a silicate of nickel and magnesium, found in New Caledonia. In the former case, the ore is roasted, smelted, and finally bessemerized. The resulting alloy of copper and nickel is much used for sheet-metal work (**Monel metal,** approx. 1 : 1). Pure nickel is separated from the copper by an electrolytic process (p. 511), or by the Monde process (see below).

The metal is white, with a faint tinge of yellow, is very hard, and takes a high polish (m.-p. 1452°). It is used in making alloys, such as German silver (copper, zinc, nickel, 2 : 1 : 1) and the "nickel" used in coinage (copper, nickel, 3 : 1). Although in these alloys the red color of the copper is completely lost, the copper is simply dissolved, and not combined. Zinc and copper, however, give a compound Cu_2Zn_3. Nickel plating on iron is accomplished exactly like silver plating (p. 516). The bath contains an ammoniacal solution of ammonium-nickel sulphate $(NH_4)_2SO_4,NiSO_4,6H_2O$, and a plate of nickel forms the anode.

The metal rusts very slowly in moist air. It displaces hydrogen with difficulty from dilute acids; but interacts with nitric acid.

Compounds of Nickel. — The **chloride** $NiCl_2,6H_2O$ is made by treating any of the oxides with hydrochloric acid, and is green in color (when anhydrous, brown). The **sulphate** $NiSO_4,6H_2O$, which crystallizes in green, square prismatic forms at 30–40°, is the most familiar salt. **Nickelous hydroxide,** $Ni(OH)_2$, is formed as an apple-green precipitate, and when heated leaves the green **nickelous oxide** NiO. It dissolves in ammonium hydroxide, giving a complex nickel-ammonia cation. It is soluble also in salts of ammonium (*cf.* p. 525). By cautious ignition of the nitrate, **nickelic oxide** Ni_2O_3 is formed as a black powder. The oxides and salts, when heated strongly in oxygen, give the oxide Ni_3O_4. The last two oxides liberate chlorine when treated with hydrochloric acid, and give nickelous chloride. **Nickelic hydroxide** $Ni(OH)_3$ is a black precipitate formed when a hypochlorite is added to any salt of nickel. **Nickelous sulphide** is thrown down by ammonium sulphide, and behaves like cobaltous sulphide (p. 639). It forms a brown colloidal solution when excess of the precipitant is used, and is then deposited very slowly.

Addition of **dimethylglyoxime** to an ammoniacal solution of a salt of nickel gives a brilliant scarlet precipitate of **an acid salt:**

$$Ni(OH)_2 + 2(HON)_2C_2(CH_3)_2 \rightarrow 2H_2O + NiH_2[C_2N_2O_2(CH_3)_2]_2.$$

This reaction is not shown by salts of cobalt, especially if oxidation to the cobaltic condition has been permitted by contact with air.

With potassium cyanide and a salt of nickel the greenish **nickelous cyanide,** $Ni(CN)_2$, is first precipitated. This dissolves in excess of the reagent, and a complex salt $K_2Ni(CN)_4,H_2O$ (= $2KCN.Ni(CN)_2$) may be obtained from the solution. This salt is of different composition from the corresponding compounds of cobalt and of iron, and is less stable. Thus, with bleaching powder, it gives $Ni(OH)_3$ as a black precipitate. When the solution is boiled in the air no oxidation to a complex nickelicyanide occurs, and indeed no such salts are known. This fact enables the chemist to separate cobalt and nickel, for when the mixed cyanides are boiled and then treated with bleaching powder, the cobalticyanide is unaffected. With potassium nitrite and acetic acid no insoluble compound corresponding to that given by cobalt salts is formed by salts of nickel. The only known compound which could be formed, $4KNO_2,Ni(NO_2)_2$, is soluble. This action also is used for the purpose of separation. The pink color of cobalt salts and the green of nickel salts are complementary colors, so that, by using suitable proportions of the two, a colorless mixture can be produced.

When finely divided nickel, made by reducing the oxide or oxalate with hydrogen at a moderate temperature, is exposed to a stream of cold carbon monoxide, **nickel carbonyl** $Ni(CO)_4$ is formed. This is a vapor and is condensable to a colorless liquid (b.-p. 43° and m.-p. −25°). The vapor is poisonous. When heated to 150–180° it is dissociated and nickel is deposited. Cobalt forms no corresponding compound. Commercially, pure nickel is separated from copper (and cobalt) in the **Monde process** by passing carbon monoxide over the pulverized alloy, and subsequently heating the gas.

Analytical Reactions of Compounds of Cobalt and Nickel. — The cobalt ion Co^{++} is pink, and the nickelous ion Ni^{++} green. The reactions used in analysis have been described in the preceding paragraphs. With borax, cobalt compounds give a blue bead (cobaltous borate), and nickel compounds a bead which is brown in the oxidizing flame and cloudy, from the presence of gray, metallic nickel, when reduced.

Exercises. — 1. What would be the interactions of calcium carbonate when fused with sand and with clay, respectively?

2. Make equations representing, (*a*) the oxidation of ferrous chloride by air, (*b*) the hydrolysis of ferrous carbonate and the oxidation of ferrous hydroxide, (*c*) the oxidation of ferrous sulphate with excess of sulphuric acid by hypochlorous acid, (*d*) the formation of ferrous and ferric tannates (p. 634), (*e*) the reduction of ferric chloride by iron and by hydrogen sulphide, respectively, (*f*) the dry distillation of basic ferric sulphate, (*g*) the formation of ferric ferrocyanide and of ferrous ferricyanide.

3. Explain the solubility of cobaltous and nickelous hydroxide in salts of ammonium.

4. Construct equations to show the formation, (*a*) of the insoluble potassium cobaltinitrite (nitric oxide is given off), (*b*) of nickelic hydroxide from nickelous chloride and sodium hypochlorite. Remembering that the hypochlorite is somewhat hydrolyzed, explain why the precipitation in (*b*) is complete.

5. Tabulate in detail the chemical relations of the elements cobalt and nickel, with especial reference to showing the resemblances and differences.

CHAPTER XLVI

THE PLATINUM METALS

THE rarer elements of Mendelejeff's eighth group divide themselves into sets of three each. Just as iron, cobalt, and nickel have similar atomic weights and much the same specific gravity (7.8–8.8), so **ruthenium** (Ru, at. wt. 101.7), **rhodium** (Rh, at. wt. 103), and **palladium** (Pd, at. wt. 106.7) have specific gravities from 12.26 to 11.5. Similarly **osmium** (Os, at. wt. 191), **iridium** (Ir, at. wt. 193), and **platinum** (Pt, at. wt. 195.2) form a triad with specific gravities from 22.5 to 21.5. Chemically, ruthenium shows the closest resemblance to osmium, and both are allied to iron. Similarly, rhodium and iridium, and palladium and platinum are natural pairs.

The six elements are found alloyed in nuggets and particles which are separated from alluvial sand by washing. Platinum forms 60–84 per cent of the whole. The chief deposits are in the Ural Mountains, smaller amounts being found in California, Australia, Borneo, and elsewhere. The components are separated by a complex series of chemical operations.

Ruthenium and Osmium. — These metals are gray like iron, while the other four are whiter and more like cobalt and nickel. They also resemble iron in being the most infusible members of their respective sets. Both melt considerably above 2000°. They likewise resemble iron in uniting easily with free oxygen, while the other four elements do not. Ruthenium gives RuO_2 and even RuO_4, although the latter oxide is more easily obtained indirectly. Osmium gives OsO_4, **"osmic acid,"** a white crystalline body melting at 40° and boiling at about 100°. The odor and irritating effects of the vapor recall chlorine (Gk. ὀσμή, odor). The substance is not an acid, nor even an acid anhydride. The aqueous solution is used in histology, and stains tissues in consequence of its reduction by organic bodies to metallic osmium. It is affected particularly by fat. Osmic acid also hardens the material without distorting it. Osmium forms also a yellow, crystalline **fluoride**, OsF_8 (m.-p. 34.5°). It will be observed that ruthenium and osmium have a maximum valence of eight.

Rhodium and Iridium. — These metals are not attacked by *aqua regia*, while the other four are dissolved, more or less slowly. They are harder than platinum, and iridium is alloyed with this metal for the purpose of increasing its resistance to the action of acids. They resemble cobalt in having no acid-forming properties. The most familiar compounds of iridium are the complex chlorides X_3IrCl_6 (= $3XCl,IrCl_3$) and X_2IrCl_6 (= $2XCl,IrCl_4$). The solutions of the latter are red, and the acid, **chloro-iridic acid** H_2IrCl_6, is often found in commercial chloroplatinic acid H_2PtCl_6, and confers upon it a deeper color.

Palladium and Platinum. — Palladium is the only metal of this family which is attacked by nitric acid. Palladium and platinum form *-ous* and *-ic* compounds of the forms PdX_2 and PdX_4, respectively. The oxides PdO and PtO and corresponding hydroxides are basic. When quadrivalent, the metals appear chiefly in complex compounds, like $H_2.PtCl_6$ and $H_2.PdCl_6$, in which the metal is in the anion. Platinum gives also platinates derived from the oxide PtO_2.

Palladium. — This metal (m.-p. 1549°), named from the planetoid Pallas, is noted chiefly for its great tendency to absorb hydrogen. When finely divided, it takes up about 800 times its own volume. The amount absorbed varies continuously with the concentration (pressure) of the hydrogen, although not according to a uniform rule, and the product is in part at least a solid solution. When a strip of palladium is made the cathode of an electrolytic cell, over 900 volumes of hydrogen may be occluded. This absorbed hydrogen, in consequence of the catalytic influence of the metal, reacts more rapidly than does the gas, and consequently a strip of hydrogenized palladium will quickly precipitate, from solutions of their salts, copper and other metals less electropositive than hydrogen and will reduce ferric and other reducible salts:

$CuSO_4 + H_2 \rightarrow H_2SO_4 + Cu$, or $Cu^{++} + H_2 \rightarrow 2H^+ + Cu$.
$2FeCl_3 + H_2 \rightarrow 2FeCl_2 + 2HCl$, or $2Fe^{+++} + H_2 \rightarrow 2Fe^{++}$

Platinum. — This metal (dim. of Sp. *plata*, silver) is grayish-white in color, and is very ductile. At a red heat it can be welded. It does not melt in the Bunsen flame, but fuses easily in the oxyhydrogen jet (m.-p. 1755°). On account of its very small chemical activity it is used in electrical apparatus and for making wire, foil, and crucibles and other vessels for use in laboratories. It interacts with fused alkalies, giving platinates. The oxygen acids are without action upon it, but on account of the tendency to form the extremely stable complex ion $PtCl_6^{=}$ (p. 520), the free chlorine and chloride-ion in *aqua regia* convert it into chloroplatinic acid H_2PtCl_6.

The metal condenses oxygen upon its surface and it dissolves hydrogen. The finely divided forms of the metal, such as **platinum sponge** made by igniting ammonium chloroplatinate $(NH_4)_2PtCl_6$, **platinum black** made by adding zinc to chloroplatinic acid, and **platinized asbestos** made by dipping asbestos in a solution of chloroplatinic acid and heating it, show this behavior very conspicuously. They cause instant explosion of a mixture of oxygen and hydrogen, in consequence of the heat developed by the rapid union of that part of the gases which is condensed in the metal. A heated spiral of fine platinum wire will continue to glow if immersed in the mixture of methyl alcohol vapor and air (oxygen), formed by placing a little of the alcohol in the bottom of a beaker. Some cigar-lighters work on this principle. The heat is developed by the interaction between the substances, which takes place with great speed at the surface of the platinum. Platinum sponge is used as a contact agent in making sulphur trioxide (p. 279).

Platinum was the only otherwise suitable substance which had the same coefficient of expansion as glass, and it was consequently fused into incandescent bulbs and furnished the electrical connection with the filament in the interior. Recently, however, a less expensive substitute has been found. Large amounts are also consumed in photography and by dentists. It is used also in making jewelry, and in Russia for coinage. The price of the metal is subject to great variations, since a rainy season in the Caucasus will render larger amounts accessible to the miners; but, on the whole, the many applications which have been found for it have quintupled its price in the last thirty years. The price is now about twice that of gold.

When special resistance to chemical or mechanical influences is required, as in standard meters for international reference, or points of fountain pens, the alloy with iridium is employed.

Compounds of Platinum. — **Platinous chloride** is made by passing chlorine over finely divided platinum at 240–250°, or by heating chloroplatinic acid to the same temperature. It is greenish and insoluble in water, but forms with hydrochloric acid the soluble **chloroplatinous acid** H_2PtCl_4. Potassium chloroplatinite K_2PtCl_4 is used in making platinum prints. Bases precipitate black **platinous hydroxide** $Pt(OH)_2$, which interacts with acids but not with bases. Gentle heating gives the **oxide** PtO and stronger heating the metal. With potassium cyanide and barium cyanide soluble **platino-cyanides,** $K_2Pt(CN)_4,3H_2O$ and $BaPt(CN)_4,4H_2O$, are formed. These substances, when solid, show strong fluorescence (p. 606), converting X-rays as well as ultra-violet rays into visible radiations. The barium salt is used to coat screens on which the shadows cast by X-rays are received.

Chloroplatinic acid $H_2PtCl_6,6H_2O$ is made by treating the metal with *aqua regia*, and forms reddish-brown deliquescent crystals. With potassium and ammonium salts, it yields the sparingly soluble, yellow chloroplatinates K_2PtCl_6 and $(NH_4)_2PtCl_6$ (*cf.* p. 452), in solutions of which the platinum migrates towards the anode and silver salts precipitate Ag_2PtCl_6 and not silver chloride. **Platinic chloride** $PtCl_4$ is made by heating chloroplatinic acid in a stream of chlorine at 360°. When dissolved in water, it combines to form $H_2.PtCl_4O$, with the platinum in the negative ion. Bases interact with chloroplatinic acid, giving a yellow or brown precipitate of **platinic hydroxide** $Pt(OH)_4$. This substance interacts with bases to give **platinates,** like $Na_2H_{10}Pt_3O_{12},H_2O$. Both sets of platinum compounds interact with hydrogen sulphide, giving the **sulphides** PtS and PtS_2, respectively. These are black powders which dissolve in yellow ammonium sulphide solution, much as do the sulphides of gold, arsenic, and other metals, giving ammonium sulphoplatinates.

APPENDIX

I. The Metric System

Length. 1 meter (1 m.) = 10 decimeters = 100 centimeters (100 cm.) = 1000 millimeters (1000 mm.).

1 kilometer = 1000 meters (1000 m.) = 0.6214 miles.
1 decimeter = 0.1 m. = 10 centimeters = 3.937 inches.
1 meter = 1.094 yards = 3.286 ft. = 39.37 in.

Volume. 1 liter = 1000 cubic centimeters (1000 c.c.) = a cube 10 cm. × 10 cm. × 10 cm.

1 liter = 0.03532 cu. ft. = 61.03 cu. in. = 1.057 quarts (U. S.) or 1.136 quarts (Brit.) = 34.1 fl. oz. (U. S.) = 35.3 oz. (Brit.).

1 fl. ounce (U. S.) = 29.57 c.c. 1 ounce (Brit.) = 28.4 c.c.
1 cu. ft. = 28.32 liters.

Weight. 1 gram (g.) = wt. of 1 c.c. of water at 4° C. 1 kilogram = 1000 g.

1 gram = 10 decigrams = 100 centigrams (100 cgm.) = 1000 milligrams (1000 mgm.).

1 kilogram = 2.205 lbs. avoird. (U. S. and Brit.).
1 lb. avoird. = 453.6 g.
1 oz. avoird. (U. S. and Brit.) = 28.35 g. 100 g. = 3.5 oz.
1 nickel (U. S.) weighs 5 g. 1 halfpenny (Brit.) weighs 5 to 5.7 g.

II. Scale of Hardness

Each of the following minerals will scratch the surface of a specimen of any one *preceding* it in the list.

1. Talc
2. Gypsum (or NaCl)
3. Calcite (or Cu)
4. Fluorite
5. Apatite
6. Felspar
7. Quartz
8. Topaz
9. Corundum
10. Diamond

Glass is slightly scratched by 5, and easily by those following. Glass will not scratch 5 distinctly, but will scratch those preceding 5.

A good **knife** scratches 6 slightly, but not those following.

A **file** will scratch 7, but not those following.

III. Temperatures Centigrade and Fahrenheit

Upon the centigrade scale, the freezing-point of water is 0° C. and the boiling-point 100° C. Upon the Fahrenheit scale, the same points are 32° F. and 212° F., respectively. The same interval is thus 100° on the one scale and 180° on the other. The degree Fahrenheit is therefore $\frac{100}{180}$ or $\frac{5}{9}$ of 1° Centigrade. Any temperatures can be converted by using the formulæ:

$$\text{C.}^\circ = \tfrac{5}{9}\,(\text{F.}^\circ - 32), \qquad \text{F.}^\circ = \tfrac{9}{5}\,(\text{C.}^\circ) + 32.$$

The following table (IV) contains the temperatures from 0° C. to 35° C., with the corresponding values on the Fahrenheit scale (32° F. to 95° F.).

IV. Vapor Pressures of Water

Both the Fahrenheit (F.) or ordinary and the Centigrade (C.) temperatures are given.

Temperature.		Pressure, mm.	Temperature.		Pressure, mm.
F.	C.		F.	C.	
32°	0°	4.6	71.6°	22°	19.7
41	5	6.5	73.4	23	20.9
46.4	8	8.0	75.2	24	22.2
48.2	9	8.6	77.0	25	23.6
50.0	10	9.2	78.8	26	25.1
51.8	11	9.8	80.6	27	26.5
53.6	12	10.5	82.4	28	28.1
55.4	13	11.2	84.2	29	29.8
57.2	14	11.9	86.0	30	31.5
59.0	15	12.7	87.8	31	33.4
60.8	16	13.5	89.6	32	35.4
62.6	17	14.4	91.4	33	37.4
64.4	18	15.4	93.2	34	39.6
66.2	19	16.3	95.0	35	41.8
68.0	20	17.4	.....	...	.....
69.8	21	18.5	212.0	100	760.0

V. Order of Activity of the Metals

(Electromotive Series)

Each metal, when placed in a solution of a salt of one of the metals *following* it in the list, displaces the second metal and deposits it in the free condition (see pp. 60, 260, 438, 531).

For explanation of potential differences (electromotive series), see pp. 539–547.

Potassium
Sodium
Barium
Strontium
Calcium
Magnesium
Aluminium
Manganese
Zinc
Chromium
Cadmium
Iron
Cobalt
Nickel
Tin
Lead
Hydrogen
Copper
Arsenic
Bismuth
Antimony
Mercury
Silver
Palladium
Platinum
Gold

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*** Acids are all listed under "acid" and salts under the positive radical.

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TABLE OF THE PERIODIC SYSTEM

E^0	E^ICl E_2^IO	$E^{II}Cl_2$ $E^{II}O$	$E^{III}Cl_3$ $E_2^{III}O_3$	$E^{IV}H_4$ $E^{IV}O_2$	$E^{III}H_3$ $E_2^VO_5$	$E^{II}H_2$ $E^{VI}O_3$	EH $E_2^{VII}O_7$	$E^{VIII}O_4$.
He=4 Ne=20.2	Li=7 Na=23	Gl=9 Mg=24.3	B=11 Al=27	C=12 Si=28.3	N=14 P=31	O=16 S=32	F=19 Cl=35.5	. . . .
A=39.9	K=39 Cu=63.6	Ca=40 Zn=65.4	Sc=44 Ga=70	Ti=48 Ge=72.5	V=51 As=75	Cr=52 Se=79.2	Mn=55 Br=80	Fe=56 Co=59 Ni=58.7
Kr=83	Rb=85.4 Ag=108	Sr=87.6 Cd=112.4	Y=89 In=115	Zr=90.6 Sn=119	Cb=93.5 Sb=120	Mo=96 Te=127.5	. . . . I=127	Ru=101.7 Rh=103 Pd=106.7
Xe=130	Cs=133 Au=197	Ba=137.4 Hg=200.6	La=139 Tl=204	Ce, etc., 140-174 Pb=207	Ta=181.5 Bi=208.5	W=184	. . . .	Os=191 Ir=193 Pt=195
Nt=222.4	. . . .	Ra=226	. . . .	Th=232.4	. . . .	U=238.2	. . . .	. . . .

In this table atomic weights are given in round numbers.

INTERNATIONAL ATOMIC WEIGHTS (1917)

		O = 16.			O =
inium	Al	27.1	Molybdenum	Mo	9
nony	Sb	120.2	Neodymium	Nd	14
n	A	39.88	Neon	Ne	2
ic	As	74.96	Nickel	Ni	5
m	Ba	137.37	Niton (radium emanation)	Nt	22
uth	Bi	208.0	Nitrogen	N	1
n	B	11.0	Osmium	Os	19
ine	Br	79.92	Oxygen	O	1
nium	Cd	112.40	Palladium	Pd	10
ium	Cs	132.81	Phosphorus	P	31.04
um	Ca	40.07	Platinum	Pt	195.2
on	C	12.005	Potassium	K	39.10
m	Ce	140.25	Praseodymium	Pr	140.9
rine	Cl	35.46	Radium	Ra	226.0
mium	Cr	52.0	Rhodium	Rh	102.9
lt	Co	58.97	Rubidium	Rb	85.45
mbium	Cb	93.1	Ruthenium	Ru	101.7
er	Cu	63.57	Samarium	Sa	150.4
rosium	Dy	162.5	Scandium	Sc	44.1
m	Er	167.7	Selenium	Se	79.2
pium	Eu	152.0	Silicon	Si	28.3
rine	F	19.0	Silver	Ag	107.88
linium	Gd	157.3	Sodium	Na	23.00
um	Ga	69.9	Strontium	Sr	87.63
anium	Ge	72.5	Sulphur	S	32.06
inum	Gl	9.1	Tantalum	Ta	181.5
	Au	197.2	Tellurium	Te	127.5
m	He	4.00	Terbium	Tb	159.2
nium	Ho	163.5	Thallium	Tl	204.0
rogen	H	1.008	Thorium	Th	232.4
m	In	114.8	Thulium	Tm	168.5
e	I	126.92	Tin	Sn	118.7
m	Ir	193.1	Titanium	Ti	48.1
	Fe	55.84	Tungsten	W	184.0
ton	Kr	82.92	Uranium	U	238.2
hanum	La	139.0	Vanadium	V	51.0
	Pb	207.20	Xenon	Xe	130.2
um	Li	6.94	Ytterbium (Neoytterbium)	Yb	173.5
cium	Lu	175.0	Yttrium	Yt	88.7
nesium	Mg	24.32	Zinc	Zn	65.37
ganese	Mn	54.93	Zirconium	Zr	90.6
ury	Hg	200.6			